SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
FIAT LVX
MDCCCLXVIII
EX LIBRIS

CHEMISTRY

OF

COMMON THINGS

BY

RAYMOND B. BROWNLEE
STUYVESANT HIGH SCHOOL

ROBERT W. FULLER
STUYVESANT HIGH SCHOOL

WILLIAM J. HANCOCK
ERASMUS HALL HIGH SCHOOL

JESSE E. WHITSIT
DE WITT CLINTON HIGH SCHOOL

ALL OF NEW YORK CITY

ALLYN AND BACON
Boston New York Chicago

QD37
B7

COPYRIGHT, 1914, BY
RAYMOND B. BROWNLEE, ROBERT W. FULLER,
WILLIAM J. HANCOCK, AND JESSE E. WHITSIT.

321405

Norwood Press
J. S. Cushing Co. — Berwick & Smith Co.
Norwood, Mass., U.S.A.

PREFACE

As the title indicates, this book deals with the chemistry of everyday affairs. It is designed to meet the growing demand that high school courses should prepare the pupil for citizenship. In other words, the book is planned for that large number of students who are limited to a single course in chemistry. The facts and principles of such a course should be of practical use throughout life.

In an endeavor to meet the varying needs of such students, a wide range of topics has been treated. This will enable the teacher to select a course best suited to the requirements of his community. To this end, particular attention has been given to the chemistry needed for the first courses in industrial, technical, and agricultural schools, as well as in those teaching domestic science.

It is expected that most schools will cover Part I, as this deals with such fundamental ideas and principles as chemical changes; acids, bases, and salts; weight relations; chemical nomenclature; solution; oxidation and combustion. Moreover, Part I contains practical topics of universal interest, such as the chemistry of heating and lighting; air and ventilation; water and its purification; properties of metals; and food values.

Part II supplies additional material for courses adapted to special needs. The authors have striven to group a large amount of interesting information around scientific principles, and to make it both usable and scientifically accurate. From this second part, the teacher can select the chapters best adapted to the needs of his particular school.

No apology is offered for the omission from this Chemistry of Common Things of certain theoretical topics, traditional to

321445

a first course in chemistry. Furthermore, the aims of this book have rendered necessary a departure from the familiar systematic study according to elements and their compounds. The authors believe, however, that the method of treatment has a sound scientific basis, and puts the chemistry of common life into a form at once attractive and useful.

New York,
November, 1914.

ACKNOWLEDGMENTS

The authors have been materially assisted in the preparation of this book, and particularly in the matter of securing material for illustrations, by the courtesy of members of the teaching profession, of artists, and of manufacturers. Credit for copyrighted pictures will be found in connection with the pictures themselves. We are under especial obligation to Mr. H. B. Judy, of the Brooklyn Institute of Arts and Sciences, and to Mr. George Wright, of Westport, Conn., for drawings; to the American Museum of Natural History, New York, and to Professor L. H. Merrill, of the University of Maine, for photomicrographs; to Professor G. E. Whipple, of Harvard University, for data and illustrations of water purification; and to Professor H. C. Sherman, of Columbia University, for data on food values.

Data and illustrative material have also been furnished by our associates, Messrs. C. D. Griswold, L. J. San, Ernst Schwarzkopf, and W. C. Uhlig, of the Stuyvesant High School, and Mr. B. M. Jaquish, of the Erasmus Hall High School. Particular mention should be made of information and drawings relating to the use of illuminating gas for light and fuel supplied by the Consolidated Gas Company of New York, and information on aluminum furnished by the Everwear Aluminum Company. To all of these gentlemen we extend our hearty thanks.

Grateful acknowledgment is made to the following manufacturers for illustrations furnished by them: Blaugas Company of America; Blaw Steel Construction Company, Pittsburg; Brooklyn Union Gas Company; Carborundum Company; Crucible Steel Company of America; Dairy Products Machine Construction Company, Derby, Conn.; Eimer and Amend, New York; Goldschmidt Thermit Company; Dr. Paul Heroult, New York; International Acheson Graphite Company; International Oxygen Company, New York; Isbell-Porter Company, Newark, N. J.; National Transit Company, Oil City, Pa.; Oxweld Acetylene Company, Newark, N. J.; Oxy-Acetylene Appliance Company, New York; Prest-O-Lite Company; Retsof Mining Company, Retsof, N. Y.; Ringen Stove Company, St. Louis; Simplex Automobile Company; Standard Oil Company.

CONTENTS

PART ONE

CHAPTER PAGE

I. Chemical Action 1

II. Direct Combination 8

III. Acids 14

IV. Bases 23

V. Salts 33

VI. Weight Relations 44

VII. Nomenclature and Valence 55

VIII. Writing of Chemical Equations 66

IX. Solutions 76

X. Burning and Oxidation 91

XI. Fuels 101

XII. Fireplaces and Stoves 114

XIII. Gas and Gasoline Stoves 122

XIV. Oil and Gas Lights 132

XV. Air and Ventilation 144

XVI. Chemical Purification 157

XVII. Water 167

XVIII. Typical Properties of Metals 192

XIX. Carbon Compounds 205

Hydrocarbons, Substitution Products, and Alcohols.

XX. Carbon Compounds 222

Aldehydes, Acids, Esters, and Carbohydrates.

XXI. Foods 242

PART TWO

CHAPTER		PAGE
XXII.	The Cooking and the Adulteration of Foods	260
XXIII.	Bread Making	267
XXIV.	Milk	278
XXV.	Cream, Ice Cream, Butter, and Cheese	293
XXVI.	Cleaning and Laundering	302
XXVII.	Ink	314
XXVIII.	Textile Materials	322
XXIX.	Dyes and Dyeing	336
XXX.	Photography	344
XXXI.	Paints, Oils, and Pigments	353
XXXII.	Distillation of Petroleum, Wood, and Coal	368
XXXIII.	Blast Lamps and Blowpipes	385
XXXIV.	Gas Engines	396
XXXV.	Extraction of Metals	403
XXXVI.	Electric Furnaces	417
XXXVII.	Electrochemistry	430
XXXVIII.	Corrosion of Metals	452
XXXIX.	Cleaning of Metals	461
XL.	Iron and Steel	468
XLI.	Lime, Cement, and Building Materials	490
XLII.	Brick and Pottery	506
XLIII.	Glass	516
XLIV.	Commercial Chemicals	533
XLV.	Agriculture	562
XLVI.	Chemical Calculations	588

Physical Constants of the Important Elements . . . 600

Index 603

CHEMISTRY OF COMMON THINGS

CHAPTER I

CHEMICAL ACTION

1. Chemical Change. — A piece of wood burns in an open fire and there is apparently nothing left but ashes. Fruit that is picked green often ripens, and then decays if kept too long. Milk becomes sour on standing. Silver and brass tarnish. Cider left exposed to the air changes to vinegar. Whichever way we turn, we see things changing their nature. The change of one substance into another is called a *chemical change*. To investigate and explain these changes is the object of Chemistry. The above changes are quite complex, so, before attempting to

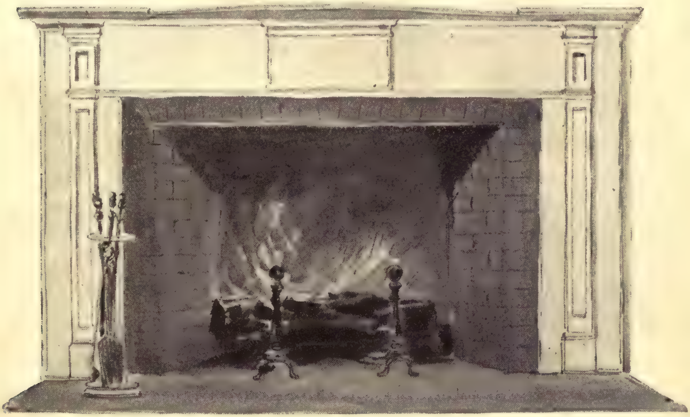


FIG. 1. — A WOOD FIRE.

explain them, we will take up some simpler types of chemical change.

2. Decomposition of Mercuric Oxide. — The simplest type of chemical change is that in which one material is broken up into two new materials. Let us take a little of the red powder called mercuric oxide and heat it in a test tube. As the heating continues, we notice on the cooler portions of the tube drops of a silvery white liquid, which we recognize as quicksilver or *mercury*. While the heating is still going on, we plunge a glowing splinter of wood into the tube above the red powder, and the splinter bursts into flame. As the spark only *glowed* in ordinary air, the gas in the tube must be different from air. It is oxygen, a gas which forms a fifth of ordinary air. No one has ever been able to get anything but mercury out of mercury, or anything but oxygen out of oxygen. The red powder consisted, therefore, of a silvery metallic liquid and a colorless gas. We have changed the mercuric oxide into other things with different properties, and so the change is a chemical change. This kind of change, in which a substance is broken up into simpler substances, is called *decomposition*.

3. Decomposition of Water. — Water is the most familiar chemical compound that we have. We know it in three forms, gaseous water (steam), liquid water, and solid water (ice). We know that no ordinary heating will break water up into simpler substances, for it simply changes into steam, which may be again condensed to liquid water. Decomposition in the case of water, as in many instances, may be brought about by the use of electricity. Since pure water is not a conductor of electricity, it is necessary to add some substance, such as sulphuric acid or caustic soda, which will make a conducting solution. The original amount of the substance added remains at the end of the process, so it is really the water that is decomposed by the current.

The water may be placed in the apparatus shown in Fig. 2. When the current is passed, a cloud of fine bubbles surrounds each electrode, but there is a larger cloud around the plate through which the current leaves the solution. This plate is called the *cathode*, which means the "way out." Each gas may be separately collected by allowing it to bubble up into tubes, previously filled with water, and placed over the ends of the electrodes. The gas, as it enters each collecting tube, displaces some of the water. Observing the rate at which the gases collect, we find that the gas at the cathode is liberated twice as fast as that at the other electrode — the *anode*. Both gases are colorless, and so we cannot distinguish them by their appearance. But if we apply a flame to the gas in the cathode tube, we find that it ignites with a slight explosion and burns with a pale, almost invisible blue flame. This gas is called *hydrogen*. On bringing a lighted match or splinter to the mouth of the other tube, there is no explosion and the gas does not burn. When the burning splinter is inserted in the tube, it is seen to burn more brightly; a splinter that is merely glowing will burst into flame. This gas we recognize as

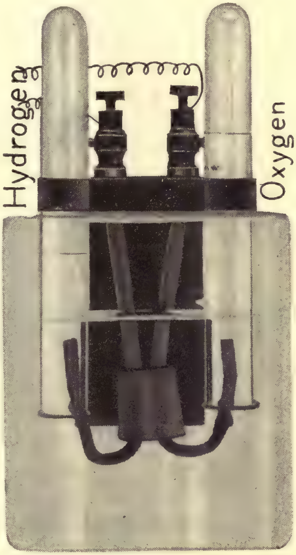
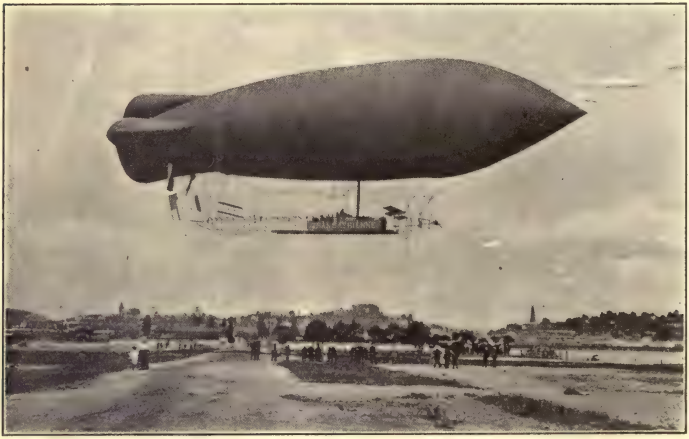


Fig. 2. — Electrolysis of Water.

oxygen, the same gas which was liberated in the heating of mercuric oxide. When water is decomposed by electricity, hydrogen is liberated at the cathode and oxygen at the anode; the volume of the hydrogen is twice that of the oxygen.[1] By continuing the process long enough, all the water in the tube could be decomposed, showing that water consists of hydrogen and oxygen only.



By courtesy of *The Scientific American*.

FIG. 3. — DIRIGIBLE BALLOON.

4. Properties of Hydrogen. — As these gases are very important chemical substances, we will examine their properties more fully. Hydrogen is the lightest gas known, being more than fourteen times as light as air. It burns in air with a transparent blue flame which is often difficult to distinguish. When mixed with half its volume of oxygen and ignited, the mixture explodes with fearful violence. Water results from the combination of the two gases. Mixtures of hydrogen and air, when lighted, explode with different degrees of violence. The flame of burning hydrogen is one of the hottest known. This flame may be produced safely by means of the oxy-hydrogen blowpipe. The blowpipe consists of two concentric tubes, so that the gases may be kept separate until they unite in the flame at the end. The calcium light, used in stereopticons (Fig. 4), is produced by heating a piece of lime in an oxy-hydrogen flame. Platinum and other metals having high melting points are fused by the use of this blowpipe.

---

[1] For a fuller discussion of the electrolysis of water see Chapter XXXVII.

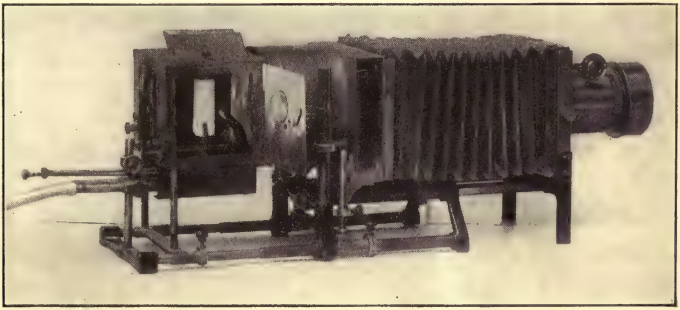


FIG. 4. — STEREOPTICON WITH CALCIUM LIGHT.

5. Properties of Oxygen. — Oxygen is heavier than hydrogen. It is about one ninth heavier than air. Oxygen is slightly soluble in water — to a sufficient extent so that fish obtain all they need from dissolved air. Like hydrogen, oxygen has no odor. Its most striking property is the ease with which it unites with a large number of substances. All cases of ordinary burning are the uniting of oxygen with the coal, wood, oil, or other substance that is being burned. The subject of combustion will be treated fully in Chapters X to XIV.

6. Compounds and Elements. — We could take other familiar substances and break them up into simpler ones by various processes. In all such cases, we find that we always get the same component parts from a given substance, and always in the same proportion. Thus, mercuric oxide always yields mercury and oxygen, in the proportion of 25 parts by weight of mercury to 2 of oxygen. Water is always found to consist of hydrogen and oxygen in the proportion of 1 part by weight of hydrogen to 8 parts of oxygen. Water and mercuric oxide are examples of a class of substances known as *chemical compounds.* A chemical compound is a substance consisting of simpler substances, united in an unvarying proportion.

No one has ever been able to separate oxygen, hydrogen, or mercury into any simpler substances. Such substances are known as *chemical elements.* An element is a substance that has not yet been decomposed into simpler substances. There are about 80 elements, from which all chemical compounds are made.

SUMMARY

A Chemical Change is a change in the nature of a substance.

Decomposition is the change of a substance into simpler substances.

Water may be decomposed by electricity into the gases hydrogen and oxygen.

Hydrogen is the lightest gas known and burns with a very hot flame in oxygen or in air.

Oxygen is slightly heavier than air. Ordinary combustion is the uniting of oxygen with fuel.

A Chemical Compound is a substance consisting of elements united in unvarying proportion.

A Chemical Element is a substance which has not yet been decomposed into simpler substances.

EXERCISES

1. Give five examples of chemical change not mentioned in the chapter.

2. Describe a test by which a gas may be recognized as oxygen.

3. Tin when heated in air changes into a white powder. What kind of a change has taken place?

4. To determine the direction of current in a circuit to be used for charging a storage battery, the wires are dipped into acidulated water. How can the anode and cathode wires be distinguished by observing the result?

5. Why is hydrogen useful for filling balloons?

6. Why is it dangerous to light the gas issuing from a hydrogen generator before all the air is out of the apparatus?

7. Describe the oxy-hydrogen blowpipe and give two purposes for which it is used.

8. Fish will not live in water that has been boiled and cooled. Why?

9. Distinguish clearly between an element and a compound.

CHAPTER II

DIRECT COMBINATION

Direct Combination takes place in the familiar phenomenon of burning. It was not until a study had been made of simple cases of direct combination, similar to those described below, that a knowledge was obtained of the part played by the oxygen of the air in ordinary burning.

7. Mercury and Iodine. — When a little mercury is placed in a porcelain mortar with a small quantity of iodine, the two substances do not lose their identity but remain side by side unchanged. If, now, the mixture is rubbed vigorously with the pestle, a red substance, which resembles neither mercury nor iodine, is formed. This new substance is mercuric iodide:

$$\underset{200}{\text{mercury}} + \underset{127}{\text{iodine}} \rightarrow \underset{327}{\text{mercuric iodide}}$$

The number beneath the name of each substance represents the number of parts by weight of that substance taking part in the reaction.

8. Copper and Sulphur. — Copper is a reddish-brown element. When clean it reflects light in a manner similar to gold, silver, nickel, aluminum, and other elements called metals. This brilliancy is one of the characteristics of a metal and is called metallic luster. When in thin strips, copper may be easily bent. Sulphur is a yellow, brittle element which melts at a temperature only a few degrees above that of boiling water. When a small quantity of sulphur is placed in a test tube and held over the flame of a Bunsen burner, it first melts and later commences to boil. If a strip of thin sheet copper is thrust into the vapor of boiling sulphur, it becomes red-hot. On removing the strip, it is found to have a blue-black color, to possess a dull luster, and to be very brittle. The strip no longer possesses the characteristic properties of copper; neither does it resemble sulphur. The copper and sulphur have united chemically to form a new kind of matter, copper sulphide:

$$\begin{array}{ccccc} \text{copper} & + & \text{sulphur} & \rightarrow & \text{copper sulphide} \\ 63.6 & & 32 & & 95.6 \end{array}$$

9. Tin and Oxygen. — Tin, heated in oxygen or in air, unites with the oxygen to form a new substance, tin oxide, which, when pure, has a nearly white color.

$$\begin{array}{ccccc} \text{tin} & + & \text{oxygen} & \rightarrow & \text{tin oxide} \\ 119 & & 2 \times 16 & & 151 \end{array}$$

10. Simple Types of Burning. — Many substances when heated in air take fire and burn with a flame. A piece of magnesium ribbon when held in a flame becomes hot, and, when a definite temperature is reached, suddenly bursts into a flame of dazzling brilliancy. In place of the magnesium, a white solid appears. This new substance may be easily crushed between the fingers. As the new compound has exactly the properties of the compound formed when magnesium is burned in oxygen, and is formed only when oxygen is present, it is known to consist of magnesium in chemical combination with oxygen:

$$\begin{array}{ccccc} \text{magnesium} & + & \text{oxygen} & \rightarrow & \text{magnesium oxide} \\ 24 & & 16 & & 40 \end{array}$$

Phosphorus takes fire at a much lower temperature than magnesium. Yellow phosphorus will ignite if left exposed to the air. For this reason it is kept under water, from which it should never be removed by the bare hands. Red phosphorus takes fire less readily than yellow phosphorus and is stored dry in bottles. When phosphorus burns, the chemical action is due to the combination of phosphorus with oxygen to form a white solid, phosphorus pentoxide:

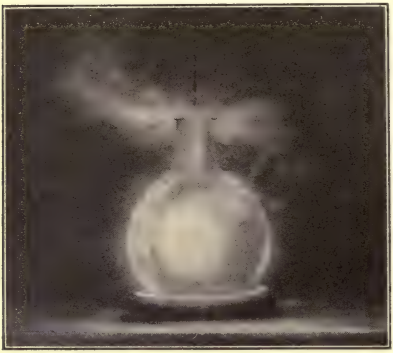


Fig. 5. — Phosphorus combining with Oxygen.

phosphorus + oxygen → phosphorus pentoxide
31 5×16 111
80

When carbon burns in air, it unites with the oxygen present to form carbon dioxide:

carbon + oxygen → carbon dioxide
12 2×16 44
32

11. Ordinary Burning. — Substances used for fuel consist either of nearly pure carbon, or of compounds containing carbon and hydrogen, or compounds containing carbon, hydrogen, and oxygen. Hard coal, coke, and charcoal are nearly pure carbon; burning oils are mixtures of compounds of carbon and hydrogen; illuminating and fuel gases consist of various mixtures of hydrogen, compounds of hydrogen and carbon, and carbon monoxide; wood consists largely of carbon in combination with hydrogen and oxygen. The chemical changes that take place when these substances are burned are in every instance similar to the simple types of burning described above. The oxygen of the air unites with the carbon and hydrogen of the fuel to form carbon dioxide and steam. It is a fortunate provision of nature that carbon dioxide is a gas, because about two and a half tons of carbon dioxide are formed when a ton of hard coal is burned. If this remained in the stove or furnace instead of passing out of the chimney, the use of coal as a fuel would be practically impossible. Since nearly four fifths of air consists of gases which do not support combustion, substances burn much more readily in pure oxygen than they do in air.

12. Synthesis. — The building of chemical compounds is called *synthesis*. The compounds mercuric iodide, copper sulphide, and the oxides just mentioned, were synthesized from their elements. In many cases, the desired compound is built from simpler compounds.

SUMMARY

Mercury and Iodine unite, when vigorously rubbed together, to form the chemical compound mercuric iodide. This compound contains 200 parts by weight of mercury in combination with 127 parts by weight of iodine.

Copper Sulphide is formed when a thin strip of copper is thrust into the vapor of boiling sulphur.

Tin Oxide is formed when tin is heated to a high temperature in oxygen or in air. **Magnesium Oxide** is formed when magnesium burns in either oxygen or air. **Oxides of Phosphorus and Carbon** are also readily formed by direct combination. **In all of these cases the elements unite in fixed proportions by weight.**

Two Forms of Phosphorus are common; namely, red phosphorus and yellow phosphorus. These have different properties due to a difference in their energy content and not to the kind of matter they contain.

In Ordinary Burning, the elements contained in the fuel, chiefly carbon and hydrogen, unite with the oxygen of the air to produce the compounds carbon dioxide and steam. As these compounds are colorless, they generally pass into the air unnoticed. The presence of smoke means that a portion of the fuel is not being burned. About $2\frac{1}{2}$ tons of carbon dioxide are formed for each ton of coal burned. Nearly $\frac{4}{5}$ of air consists of gases which do not enter into combination with the fuel when it burns.

Synthesis is the building of compounds from elements, or from simpler compounds. A synthetic compound is one that has been prepared by man from less complex substances.

EXERCISES

1. Give several illustrations of direct combination.

2. What evidence is there that a new kind of matter is formed when mercury and iodine are rubbed together?

3. How does the compound formed when copper burns in sulphur differ from a mixture of the two elements?

4. Calculate the number of parts by weight of mercury that would unite with 1 part by weight of iodine.

5. How many parts by weight of iodine combine with 25 parts by weight of mercury?

6. How many pounds of sulphur would combine with 63.6 pounds of copper to form the compound copper sulphide?

7. How many pounds of sulphur would unite with 1 pound of copper? With 5 pounds?

8. Why was not the phenomenon of burning understood until the balance was used in connection with chemical experiments?

9. How would you show that ordinary burning is caused by the fuel entering into chemical combination with the oxygen of the air?

10. Can burning ever take place without the presence of oxygen? Why do you think so?

11. Why is it that matter appears to be destroyed when wood or coal burns?

12. If magnesium were as cheap as coal, why would it still be practically impossible to use it as a fuel?

13. Name an element that exists in more than one form and tell about some of the ways in which the forms differ.

14. Why does the same element sometimes show very different properties?

15. Why should not yellow phosphorus be handled with the bare hand?

16. What is the meaning of the word synthesis? Synthesis of a sentence? Synthesis of a chemical compound?

17. Can oxygen be prepared by synthesis? Explain.

18. What is synthetic camphor?

19. Why has synthetic indigo largely displaced the natural product?

20. Why have much time and money been devoted to the production of synthetic rubber?

CHAPTER III

ACIDS

THE nickeled parts of gas stoves become worn and rusty in use. Such parts are sometimes removed, cleaned, and dipped in a vat containing a solution of copper sulphate in order to coat the worn portions with copper. Then nickel is plated on the copper coating. Gold and silver may be recovered from plating solutions by placing certain metals in the solutions. These actions depend upon the replacement of one metal by another. To understand the action of an acid, we must appreciate what happens when one element replaces another.

13. Simple Replacement. — A lead compound known as lead nitrate may be made by dissolving lead in nitric acid. When a bright strip of zinc is suspended in the water solution of such a compound, the surface of the zinc immediately becomes dull. Soon the strip looks thicker and longer, on account of a dark glistening substance which appears to be growing on the zinc (Fig. 6). If the solution is left undisturbed, the dark deposit may project downward some distance into the solution. It is seen to consist of dark glistening scales arranged in a branching, treelike form. The deposit may be easily shaken or scraped from the strip, and when removed from the solution is in a dark, pulpy mass. It can, however, be readily squeezed into smaller bulk and changed by a few taps of a hammer into a metallic strip. This strip is very heavy for its size, can be easily cut by a knife, and can be readily melted to a silvery liquid. All these properties enable us to identify the substance as lead. The glistening scales which appear on the suspended zinc are nothing more nor less than lead in crystalline form.

An examination of the zinc strip shows that it is thinner than before. Its former smooth surface is rough and pitted. Weighings show that the strip is not so heavy as when it was first placed in the solution of the lead compound. Certain chemical tests prove that there is a zinc compound in the solution where only a lead compound was present originally. This shows that some of the metallic zinc went into solution at the same time that lead was being deposited. We may say that zinc is gradually replacing the lead in the solution, or, more exactly, that the zinc has taken the place of the lead in the dissolved compound, forming a similar zinc compound. This may be expressed:

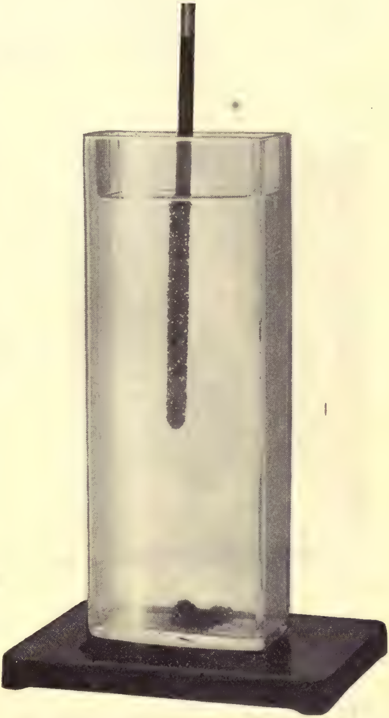


FIG. 6. — REPLACEMENT OF LEAD BY ZINC.

lead compound + zinc → zinc compound + lead

That is, a metal in a compound has been replaced by another metal. Such a replacement of one element by another element is known as a *simple replacement.* There are many instances of simple replacement where one metal replaces another. Some of the replacements are of great industrial value. Copper of the copper compounds in the waste waters of copper mines is saved by the use of scrap iron. Silver is often recovered from its solutions by the aid of copper (Fig. 7).

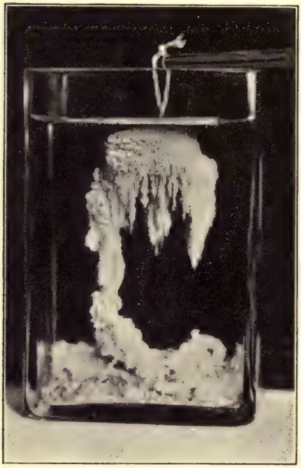


FIG. 7. — SILVER TREE.

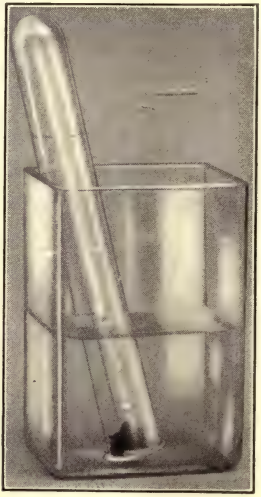


FIG. 8. — REPLACEMENT OF HYDROGEN IN ACID.

14. Acids. — It must not be thought that every simple replacement means the replacement of one metal by another. When zinc is placed in hydrochloric acid, bubbles appear on the surface of the zinc, break loose from it, and finally rise to the surface of the liquid (Fig. 8). This stream of bubbles is due to the liberation of a gas from the acid. The gas burns with a pale blue flame, forming water as the only product of combustion. It is, therefore, hydrogen. As the hydrogen is produced from the acid, the zinc is gradually eaten away. In fact, the zinc has gone into solution, taking the place of the hydrogen, and forming a compound called zinc chloride :

$$\text{zinc} + \text{hydrochloric acid} \longrightarrow \text{zinc chloride} + \text{hydrogen}$$

Similarly, iron, magnesium, and other metals will replace the hydrogen in hydrochloric acid, or the hydrogen in sulphuric acid and many other acids. These actions are all simple replacements in which the hydrogen of an acid is replaced by a metal.

Compounds containing hydrogen which can be replaced by a metal, form a large and important class of substances known as *acids.* The possession of hydrogen replaceable by a metal is characteristic of acids. Acids also have a sour taste. Vinegar and lemons are sour because of the acids they contain. Litmus, a vegetable dye, is turned red by acids. It should be remembered, however, that *acids do not possess their characteristic properties unless dissolved in water.*

The replacement of the hydrogen of hydrochloric acid may be represented more completely as follows :

$$\text{zinc} + \text{hydrochloric acid} \longrightarrow \text{zinc chloride} + \text{hydrogen}$$

$$65 \qquad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{chlorine} & 71\end{array}\right\} 73 \qquad \left.\begin{array}{ll}\text{zinc} & 65\\ \text{chlorine} & 71\end{array}\right\} 136 \qquad 2$$

The zinc combines with the chlorine of hydrochloric acid to form zinc chloride, which remains in solution.

When zinc is placed in dilute sulphuric acid, the replacement of the hydrogen of the acid results in the formation of zinc sulphate :

$$\text{zinc} + \text{sulphuric acid} \longrightarrow \text{zinc sulphate} + \text{hydrogen}$$

$$65 \qquad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\} 98 \qquad \left.\begin{array}{ll}\text{zinc} & 65\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\} 161 \qquad 2$$

In this case, the metal combines with that part of sulphuric acid which is not hydrogen, forming zinc sulphate in solution. On the evaporation of this solution, the zinc sulphate is obtained as a white solid.

Iron sulphate is formed by the replacement of the hydrogen of sulphuric acid by iron. Such compounds as zinc chloride, zinc sulphate, and iron sulphate, which are made by the replacement of the hydrogen of an acid by a metal, are known as *salts*. The two products formed by the first action of a metal with an acid are hydrogen and a salt:

$$\text{metal} + \text{acid} \longrightarrow \text{hydrogen} + \text{a salt of the metal}$$

In many cases, the hydrogen is not given off as a gas because a second action occurs.

Acids are among the most active of chemical compounds. Many of them, as has been stated, react vigorously with metals. Concentrated sulphuric acid chars wood and paper; nitric acid attacks animal and vegetable substances; hydrofluoric acid dissolves glass. Another very important action of acids is their behavior with bases. This action will be discussed later.

15. Summary: Characteristics of Acids. —

(*a*) Acids contain hydrogen replaceable by a metal.

(*b*) Acids react with metals to form salts.

(*c*) Acids taste sour.

(*d*) Acids in water solution turn blue litmus red.

(*e*) Acids react vigorously with bases and with many other substances.

16. Common Acids and their Uses. — Acids are among the most useful of chemical compounds. The agreeable taste and the health value of many fruits are due to them. *Citric acid* is found in the juice of lemons, oranges, and grapefruit. Sour milk contains *lactic acid. Tartaric acid* is obtained from crude cream of tartar, which is deposited in wine vats during the fermentation of grape juice.

Boric or boracic acid finds wide use as a mild disinfectant, *e.g.* as an eyewash and a mouthwash. Since boric acid is but slightly soluble in cold water, and it is desirable to obtain a saturated solution for these purposes, the acid is dissolved in warm water and the solution allowed to cool. Boric acid and its salts are largely employed as food preservatives. It is generally believed that this use is undesirable, particularly in the case of milk for infants.

Tannic acid finds employment in the tanning of hides into leather, in the making of inks, and in dyeing. *Oxalic acid* is useful for cleaning copper and brass, for removing stains from wood, and in the preparation of blue print paper. In bleaching, in dyeing, in calico printing, and in the manufacture of drugs and chemicals, acids are of great value. In general, it may be stated that acids play a prominent part in many kinds of manufacturing operations.

Many people think incorrectly that all acids are colorless liquids, for the reason that acids are commonly used in water solutions. All of the acids just mentioned are solids. While many of the solid acids are white, some of them possess a distinctive color. Picric acid, used as a remedy for severe burns, has a rich yellow color.

17. Hydrochloric Acid is the colorless gas, hydrogen chloride, dissolved in water. Concentrated hydrochloric acid usually contains about one third its weight of dissolved hydrogen chloride; the other two thirds are water. Dilute hydrochloric acid is usually made by mixing one volume of concentrated acid with four or five times as much water. *Muriatic acid* is an old name for hydrochloric acid, given because the acid was made from the brine of the sea. This term is now commonly used to designate the commercial acid, which contains 33 % of hydrogen chloride.

18. Nitric Acid is the water solution of a colorless liquid, hydrogen nitrate, which is about one and a half times as heavy as water. Concentrated nitric acid usually contains a little more than two thirds by weight of the hydrogen nitrate. An old name for nitric acid is *aqua fortis* (strong water), given because of its energetic action on many substances. Dilute nitric acid is made by mixing the concentrated acid with four or five times as much water.

19. Sulphuric Acid was originally made from green vitriol, a sulphate of iron, and was called *oil of vitriol.* It is an oily liquid nearly twice as heavy as water. The concentrated acid usually contains about 7 % of water, the remaining portion being the compound hydrogen sulphate. Dilute sulphuric acid is generally made by taking one volume of the concentrated acid to six volumes of water. The mixing of the liquids should be done with the greatest care to avoid accidents, as the union of the two liquids produces great heat. The concentrated acid is *slowly* poured *into water*, which is stirred constantly.

20. Acetic Acid, whose presence in a very small amount gives a sour taste to vinegar, may be bought in concentrated form known as glacial acetic acid, so named because it solidifies to an icelike solid when the temperature becomes several degrees below the ordinary room temperature. This acid contains less than 5 % of water. Commercial acetic acid contains about one third its weight of glacial acetic acid.

SUMMARY

Simple Replacement is the replacement of one element in a compound by another element. The most familiar illustrations of this are the replacement of one metal by another and the replacement of the hydrogen of an acid by a metal.

Acids are compounds containing hydrogen which can be replaced by a metal. Less important characteristics of acids are the sour taste and the turning of litmus red. An acid must be dissolved in water to show these characteristic properties. Acids react vigorously with bases and with many other substances. They are among the most useful of chemicals.

Salts are compounds formed by the replacement of the hydrogen of an acid by a metal, that combines with the part of the acid that is not hydrogen. The salt formed remains in the solution.

A Concentrated Acid is the most concentrated water solution of the hydrogen compound prepared on a large scale for commercial distribution. The amount of water varies with the particular acid; for example, concentrated hydrochloric acid contains about 60% of water; concentrated nitric acid, about 30%; and concentrated sulphuric acid, about 7%.

A Dilute Acid is usually made by mixing any volume of concentrated acid with 4 to 6 times as much water. Great care must be taken in the preparation of dilute sulphuric acid.

Acetic Acid is present in small amounts in vinegar. Glacial acetic acid contains less than 5% of water.

EXERCISES

1. What compound is formed by dissolving lead in nitric acid? How can you get the lead out of this compound?

2. State what happens when one metal replaces another in solution.

3. Write a word equation which shows how copper is recovered from the waste waters of copper mines.

4. Show how you could obtain hydrogen from sulphuric acid by simple replacement. How would you identify the hydrogen?

5. Where does the magnesium go when it is dissolved by hydrochloric acid?

6. Define an *acid.* What liquid must be present for a compound to act as an acid?

7. Write a word equation and show the weight relations for the reaction of (*a*) magnesium with sulphuric acid; (*b*) iron with hydrochloric acid. (Magnesium = 24; iron = 56.)

8. Define a *salt.* Name five salts.

9. Write the typical equation for the reaction of a metal with an acid.

10. What kind of a compound is always obtained when an acid reacts with a metal? Is hydrogen always given off?

11. Why are acids considered active compounds?

12. What simple tests would enable you to identify a liquid as concentrated sulphuric acid?

13. What is *glacial* acetic acid? Oil of vitrol? Muriatic acid? *Aqua fortis?*

14. Name three foods that contain an acid. In each case name the acid.

15. Give directions for preparing 700 c.c. of dilute sulphuric acid.

16. What are the differences between hydrogen chloride, concentrated hydrochloric acid, and dilute hydrochloric acid.

17. Are all acids liquids? Illustrate.

18. Name an acid much used by plumbers. Which one is very useful in caring for babies? Which acid is necessary to the body?

19. Why are "green apples" sour?

CHAPTER IV

BASES

21. Bases. — Bases, like acids, are very frequently encountered in everyday life. The things we know under the names of slaked lime, concentrated lye, and ammonia water belong to this class of substance.

The term *bases* is applied to a class of compounds which, in some ways, may be regarded as the opposite of acids in chemical properties. An indication of this fact is seen in their action on litmus. Water solutions of bases turn this dye from red to blue, and this fact is used as a test to distinguish soluble bases from acids.

22. Preparation of Bases. — Bases always contain a metal. They may be prepared in several ways; two of the most important are:

(*a*) by the action of metals with water;

(*b*) by the action of oxides of metals with water.

Thus, sodium hydroxide, one of the most important bases, is formed by the action of sodium with water. Sodium is a soft metal, easily cut with a knife, and having, when freshly cut, a metallic luster. It combines with oxygen and the moisture of the air so readily that it is kept under kerosene or some oil that contains no oxygen.

When sodium is placed on water, there is prompt evidence of a vigorous chemical action. The metal melts, assumes a globular form, and moves about the surface of the water rapidly. There is a hissing sound due to the liberation of a gas. This gas is hydrogen. Potassium has a similar but more violent action (Fig. 9).

The water remaining in the dish is found to have new properties; it turns red litmus blue, and has a soapy feeling. These properties are due to dissolved sodium hydroxide, which has been formed in the action. On evaporating the solution, the sodium hydroxide is seen as a white solid. This substance is composed of three elements, sodium, oxygen, and hydrogen, the last two in the proportion of 16 parts by weight of oxygen to 1 of hydrogen. Bases always contain oxygen and hydrogen, and in this proportion.

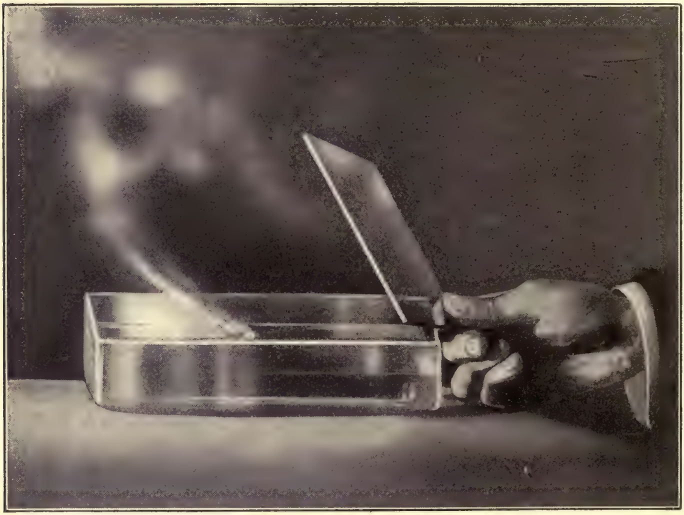


Fig. 9. — Potassium on Water.

The action of sodium with water can be represented thus:

$$\begin{array}{ccccccc} \text{sodium} & + & \text{water} & \longrightarrow & \text{sodium hydroxide} & + & \text{hydrogen} \\ 23 & & \left.\begin{array}{lr}\text{hydrogen} & 1\\ \text{oxygen} & 16\\ \text{hydrogen} & 1\end{array}\right\} 18 & & \left.\begin{array}{lr}\text{sodium} & 23\\ \text{oxygen} & 16\\ \text{hydrogen} & 1\end{array}\right\} 40 & & 1 \end{array}$$

We see that this is a replacement action. One part by weight of the hydrogen in water has been replaced by 23 parts of sodium.

Calcium, a metal somewhat resembling sodium, reacts in a similar way with water. The action is less violent, and the base, calcium hydroxide, is formed. Since it is almost insoluble in water, the calcium hydroxide can be seen as it forms:

$$\begin{array}{ccccccc} \text{calcium} & + & \text{water} & \longrightarrow & \text{calcium hydroxide} & + & \text{hydrogen} \\ 40 & & \left.\begin{array}{lr}\text{hydrogen} & 2\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\} 36 & & \left.\begin{array}{lr}\text{calcium} & 40\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\} 74 & & 2 \end{array}$$

It will be seen in both these bases that the hydrogen and oxygen are in the ratio of 1 to 16.

Most of the common metals, such as iron, copper, and zinc, do not react with water at ordinary temperatures. Hence the bases which they form cannot be obtained by the direct action of the metal with water.

23. Formation of Calcium Hydroxide. — The two bases of greatest practical importance are the two whose formation has just been described. Calcium hydroxide is a constituent of mortar and plaster. Its formation for this purpose illustrates another general method for the preparation of bases. The operation can be seen going on wherever a new building is in course of erection. To illustrate it in the laboratory, cover a few pieces of calcium oxide, *quicklime*, with water. After a time, the mixture becomes hot, indicating that a vigorous chemical action is going on. Clouds of steam arise, and the lime soon crumbles to a powder, or becomes a pasty mass if sufficient water is present:

$$\begin{array}{ccccc}
\text{calcium oxide} & + & \text{water} & \longrightarrow & \text{calcium hydroxide} \\
\left.\begin{array}{ll}\text{calcium} & 40\\ \text{oxygen} & 16\end{array}\right\} 56 & & \left.\begin{array}{ll}\text{hydrogen} & 1\\ \text{oxygen} & 16\\ \text{hydrogen} & 1\end{array}\right\} 18 & & \left.\begin{array}{ll}\text{calcium} & 40\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\} 74
\end{array}$$

This action is a direct combination. Notice again that the hydrogen and oxygen are present in the ratio of 1 to 16.

24. Importance of Bases. — Unlike acids, the majority of bases are insoluble in water. In discussing them, however, we shall confine ourselves chiefly to the soluble ones, including the slightly soluble calcium hydroxide. The insoluble bases are of comparatively little importance, but the soluble ones are among the compounds most important for the purposes of practical life.

Bases are very active substances chemically, especially with (*a*) animal and vegetable matter, (*b*) acids.

25. Action on Animal and Vegetable Matter. — Our common use of such bases as concentrated lye and ammonia water as household cleaning agents is an illustration of their power to act with animal and vegetable matter such as oils and fats, substances which do not dissolve in water. Bases act on them in such a way as to convert them into soluble substances. Hence greasy articles can be cleaned with solutions of bases.

So great is the chemical activity of some bases, however, that they cannot be used as cleaning agents on all sorts of material. In cleaning grease spots from clothing, for example, ammonia water should be used because its action is less energetic and because it readily evaporates. If sodium hydroxide were used, it would injure the material, especially if made of wool, which is quickly dissolved by concentrated solutions of bases. This strong base attacks the skin readily and should not be handled with the bare hands.

26. Soaps. — These substances are made from fats by boiling with bases. They may be regarded as the bases in modified form. They retain especially the property of dissolving oils and fats, and it is for this reason that we use them as cleaning agents where strong bases cannot be used. Cheap, coarse soaps contain a certain amount of unchanged base. It is for this reason that they roughen the hands, or injure fabrics on which they are used.

27. Alkalies. — We also use for cleaning purposes a class of substances, which, while they are not themselves bases, do the work of bases, because when dissolved in water they form a small amount of base in the solution. *Washing soda* (sodium carbonate) and borax are the most common substances used in this way. The fact that they do form bases when dissolved in water is shown by their action on litmus, which they turn from red to blue.

The term *alkali* is applied to any substance whose water solution turns red litmus paper blue. It includes soluble bases.

28. Action of Bases with Acids. — This is a very important type of action. As an illustration, consider the following experiment:

To a solution of sodium hydroxide add slowly a solution of hydrochloric acid. The mixture becomes warm, showing that a chemical action is going on. To determine when just the right amount of acid has been added, use litmus paper. Drops of the mixture are placed from time to time on litmus paper of each color. When the solution is *neutral*, neither color of paper will be affected. This act of mixing an acid with a base in the exact proportion for complete reaction with each other is termed *neutralization.* On evaporating the neutral solution, we find that a new substance, having a definite crystalline form and a characteristic taste, has been produced. This substance is sodium chloride, common table salt. Water was also formed in the reaction:

sodium + hydrochloric ⟶ water + sodium
hydroxide acid chloride

$$\left.\begin{array}{ll}\text{sodium} & 23\\ \text{oxygen} & 16\\ \text{hydrogen} & 1\end{array}\right\}40 \quad \left.\begin{array}{ll}\text{hydrogen} & 1\\ \text{chlorine} & 35.5\end{array}\right\}36.5 \quad \left.\begin{array}{ll}\text{hydrogen} & 1\\ \text{oxygen} & 16\\ \text{hydrogen} & 1\end{array}\right\}18 \quad \left.\begin{array}{ll}\text{sodium} & 23\\ \text{chlorine} & 35.5\end{array}\right\}58.5$$

Other examples of neutralization:

Sodium hydroxide and sulphuric acid form water and sodium sulphate:

sodium + sulphuric ⟶ water + sodium
hydroxide acid sulphate

$$\left.\begin{array}{ll}\text{sodium} & 46\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\}80 \quad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\}98 \quad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\}36 \quad \left.\begin{array}{ll}\text{sodium} & 46\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\}142$$

Calcium hydroxide and hydrochloric acid form water and calcium chloride:

calcium + hydrochloric ⟶ water + calcium
hydroxide acid chloride

$$\left.\begin{array}{ll}\text{calcium} & 40\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\}74 \quad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{chlorine} & 71\end{array}\right\}73 \quad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{oxygen} & 32\\ \text{hydrogen} & 2\end{array}\right\}36 \quad \left.\begin{array}{ll}\text{calcium} & 40\\ \text{chlorine} & 71\end{array}\right\}111$$

It will be noticed that water is formed in all these neutralizations. Such substances as sodium chloride, sodium sulphate, and calcium chloride are known as *salts*.

In general, acids react with bases to form (*a*) water, (*b*) a salt. This generalization is one of the most important in chemistry.

29. Summary: Characteristics of Bases.

(*a*) Bases always contain a metallic element or group of elements.

(*b*) Bases always contain hydrogen and oxygen in the ratio of 1 to 16 by weight.

(*c*) Bases in solution turn red litmus blue.

(*d*) Bases react with acids forming water and salts.

(*e*) Strong bases dissolve many oils and fats.

30. Common Bases and their Uses. — Sodium hydroxide, also called *caustic soda*, is obtained cheaply from common salt by the use of the electric current. It is the most important of all bases from a practical standpoint, because of its chemical activity and its cheapness. Its principal uses are for making soaps, bleaching compounds, and paper pulp.

Potassium hydroxide, *caustic potash*, is similar to sodium hydroxide and can be used for many of the same purposes. It is more expensive, however, and in soap making is not so desirable, as it commonly produces a soft soap. The old-fashioned homemade soft soap was made from the potash (potassium carbonate) secured from wood ashes.

Lye, or concentrated lye, is a term applied to several forms of strong bases sold commercially. The substance is either sodium or potassium hydroxide, or potassium carbonate (potash), or a mixture of these. In water solution potassium carbonate produces potassium hydroxide.

Slaked lime, described above (§ 23) as a constituent of mortar and plaster, has many other practical uses. It acts vigorously on animal and vegetable matter, like the stronger bases, and for this reason it is used on a large scale to remove hair from hides previous to tanning. It is the cheapest base obtainable, but it is not adapted to the purpose of soap making, because the products of its action with oils and fats are insoluble in water. For the same reason it cannot be used as a direct cleaning agent.

The water solution of ammonium hydroxide, sold also as *ammonia water* and as *spirits of hartshorn*, is especially adapted to certain uses because the base itself readily evaporates, or is "volatile." The substance is sometimes spoken of as the volatile alkali. It is much used as a cleaning agent, especially for fabrics, because it readily evaporates and does not remain in contact with the cloth long enough to do harm. It is also an important reagent in the chemical laboratory.

Ammonium hydroxide is an apparent exception to the statement that a base always contains a metallic element. It is formed from its elements in the following proportion: nitrogen 14 parts by weight, hydrogen 4 parts, which are combined with the usual 1 part of hydrogen and 16 parts of oxygen. The combination of 14 parts of nitrogen with 4 parts of hydrogen acts in many ways like an element. It is spoken of as a metallic group. Just as we have ammonium hydroxide, we also have many other ammonium compounds, such as ammonium chloride (sal ammoniac), ammonium sulphate, and ammonium nitrate.

SUMMARY

Bases constitute an important class of compounds that are regarded as the chemical opposites of acids. They contain a metal united to 1 part of hydrogen and 16 parts of oxygen.

Bases in solution turn litmus from red to blue. They react with acids to form a salt and water.

Alkali is a term which includes the soluble bases and many other substances that form more or less base when they are dissolved in water.

Bases and Alkalies are useful as a means of dissolving animal and vegetable matter, especially greases. The stronger ones form very powerful cleaning agents because of this property.

Soaps act like modified bases. They are made by boiling oils or fats with strong bases.

Important Soluble Bases are sodium hydroxide, potassium hydroxide, and ammonium hydroxide. Calcium hydroxide is a strong base, but is only slightly soluble in water.

Other important alkalies are sodium carbonate (washing soda) and borax.

EXERCISES

1. How would you distinguish the solution of an acid from the solution of a base?

2. Why should care be taken not to get a solution of strong base on the hands? On the clothing? What substances could be used to counteract the harmful effects? What precautions should be taken in applying these remedies?

3. What base can be applied to clothing without damage? Why? Of what practical use is this fact?

4. A base is added to the solution of an acid until the mixture no longer affects either color of litmus. What products have been formed? What general term may be applied to the process?

5. If acid were spilled on the clothing, what base would you apply? Why?

6. Why are soaps preferred to strong bases in cleaning clothing?

7. What is a base? An alkali? Name an alkali which is not a base.

8. What means could be used to quickly clean a very greasy floor? A very greasy cotton cloth? A very greasy woolen cloth?

9. Cheap soaps sometimes contain free alkali. What are the advantages and the disadvantages of such a soap?

10. Why is calcium hydroxide used instead of sodium hydroxide in removing hair from hides in the manufacture of leather?

11. How can sodium hydroxide be made in the laboratory? Write a word equation for the reaction.

12. What very common use is made of calcium hydroxide in building operations? How is it prepared for this purpose?

13. What are soaps? How are they made?

14. What substance would be used in cases where a strong, cheap base was required?

15. Why is ammonium hydroxide an apparent exception to the fact that a base always contains a metal? Explain.

CHAPTER V

SALTS

31. Sodium Chloride. — Sodium chloride, our familiar table salt, is the most typical example of a salt, as it gives its name to the whole group of compounds. It is so widely distributed that sensitive tests will show traces of it almost anywhere. Every stream carries to the ocean traces of salt dissolved in its waters. The reason for the noticeable amount of salt in the ocean and salt lakes is that the water evaporates, leaving the sodium chloride. Great beds of rock salt, formed by the evaporation of some prehistoric sea, are found deep in the earth in many

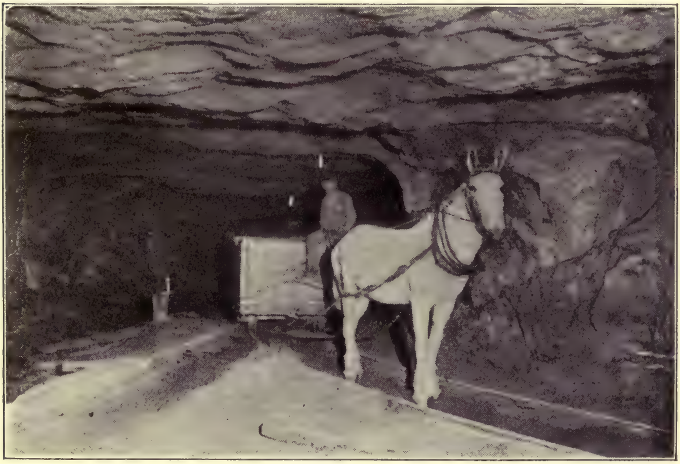


FIG. 10. — INTERIOR OF SALT MINE.

places. These salt deposits are sometimes mined, as in Poland, western New York, Michigan, and Louisiana (Figs. 10, 11). Another method of working the rock salt deposits is to drill holes to the salt beds, force water down some of the holes, thus forcing the brine formed out through others. The brine is then evaporated. Underground brine deposits are found at a few places, as at Syracuse, New York. Sea water furnishes an inexhaustible source of salt, which is separated in some countries by allowing the sun's heat to evaporate the water from shallow reservoirs (Fig. 12). In cold climates, the salt is obtained by freezing sea water, the ice being fresh and the salt remaining in a concentrated brine.

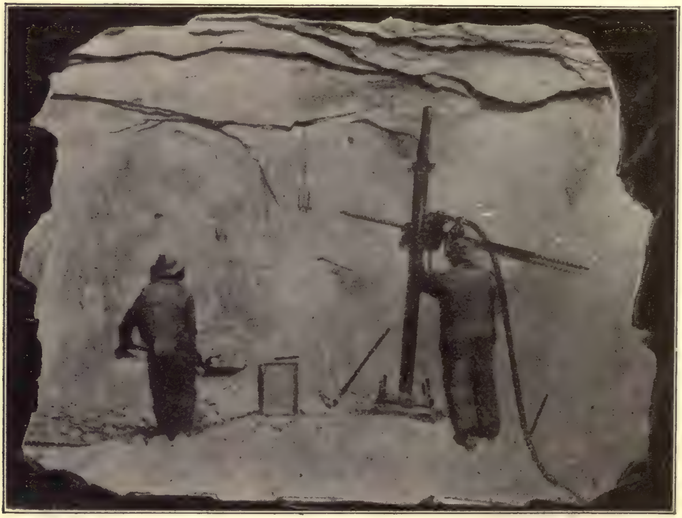
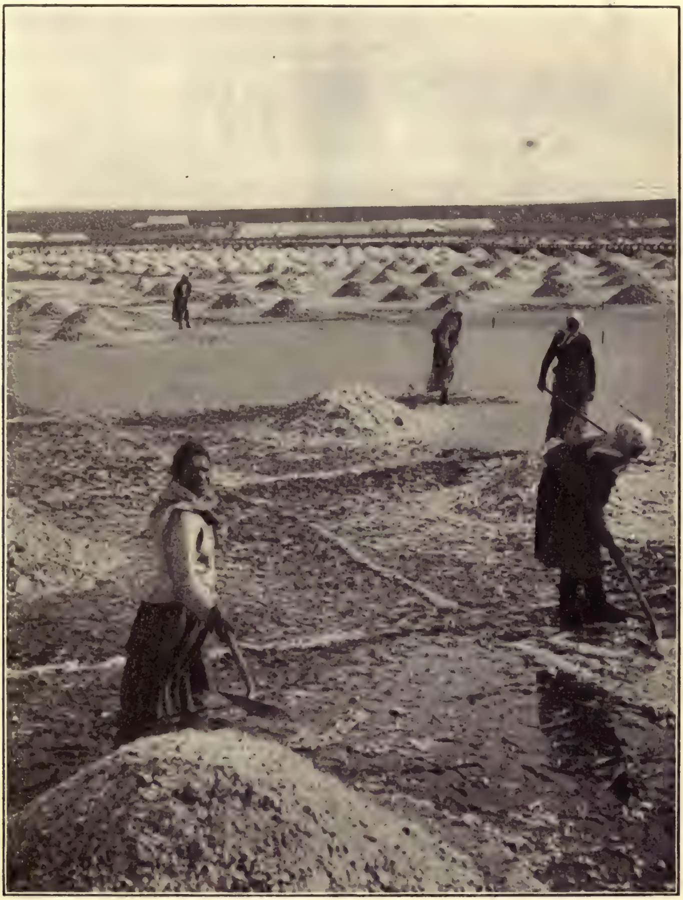


FIG. 11. — DRILLING SALT PREPARATORY TO BLASTING.

When brine is evaporated slowly, as by the heat of the sun, the resulting crystals of salt are much larger than when more rapid evaporation takes place. Table salt is evaporated at the most modern plants under very much reduced pressure, which greatly lowers the boiling point



Copyright by Underwood & Underwood.

FIG. 12. — RUSSIAN SALT FIELDS. COLLECTING SALT AFTER EVAPORATION.

and increases the economy of the process. Dairy salt is produced by slow evaporation. Rock salt (Fig. 13) as it comes from the mines is used for feeding cattle, but most of the rock salt mined is crushed, and then sold for use in freezing ice cream, preserving meat, and for the manufacture of other sodium compounds. The last-mentioned use is of enormous commercial importance, as such compounds as washing soda, baking soda, and caustic soda are manufactured from salt. Sodium chloride does not affect the color of litmus, being neutral in reaction. The caking of fine salt in damp weather is chiefly due to magnesium compounds, which absorb water from the air.

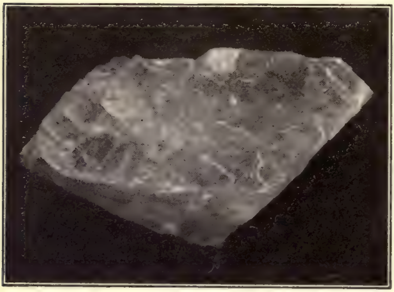


FIG. 13. — MASS OF ROCK SALT.

32. Production of Salt by Neutralization.— Pure sodium chloride may be made by neutralizing sodium hydroxide with hydrochloric acid :

$$\begin{array}{c}\text{sodium}\\ \text{hydroxide}\end{array} + \begin{array}{c}\text{hydrochloric}\\ \text{acid}\end{array} \longrightarrow \text{water} + \text{sodium chloride}$$

$$\left.\begin{array}{lr}\text{sodium} & 23\\ \text{hydrogen} & 1\\ \text{oxygen} & 16\end{array}\right\}40 \quad \left.\begin{array}{lr}\text{hydrogen} & 1\\ \text{chlorine} & 35.5\end{array}\right\}36.5 \quad \left.\begin{array}{lr}\text{hydrogen} & 2\\ \text{oxygen} & 16\end{array}\right\}18 \quad \left.\begin{array}{lr}\text{sodium} & 23\\ \text{chlorine} & 35.5\end{array}\right\}58.5$$

This method is not used commercially, since it is much more expensive than the purification of natural salt. Many other salts, however, are made by the neutralization of the base containing the metallic portion of the salt with the acid containing the non-metallic portion. For it must be remembered that one product of neutralization is always a salt (§ 28).

33. Production of Salts by the Action of Acid and Metal. — When zinc is treated with hydrochloric acid, hydrogen is liberated and the zinc replaces the hydrogen in the acid, forming *zinc chloride* (§ 14):

zinc + hydrochloric acid ⟶ zinc chloride + hydrogen

When more acid is used than is necessary to dissolve the zinc, the acid solution formed is very efficient in cleaning the surface of metals. It is frequently used as a soldering fluid, to remove the oxides from the pieces to be soldered together, so that the solder will adhere more firmly to the metal.

It will be remembered that *zinc sulphate* is produced in a similar way by the action of zinc with sulphuric acid (§ 14):

zinc + sulphuric acid ⟶ zinc sulphate + hydrogen

The zinc sulphate is obtained in transparent crystals by evaporation of the solution formed. It is often called *white vitriol.* It is used in calico printing and in electric batteries. In like manner, sodium chloride might be formed by the action of sodium with hydrochloric acid, but the action would be so violent as to be extremely dangerous. Magnesium, dropped into dilute hydrochloric acid, decomposes the acid, liberating hydrogen and taking its place to form magnesium chloride:

$$\text{sodium} + \text{hydrochloric acid} \longrightarrow \begin{matrix}\text{sodium}\\ \text{chloride}\end{matrix} + \text{hydrogen}$$

$$\text{magnesium} + \text{hydrochloric acid} \longrightarrow \begin{matrix}\text{magnesium}\\ \text{chloride}\end{matrix} + \text{hydrogen}$$

A *salt* is a product formed by the replacement of the hydrogen of an acid by a metal.

34. Action of a Metallic Oxide with an Acid. — Cold dilute sulphuric acid does not act on copper, so copper sulphate cannot be made by simple replacement. Copper oxide, however, readily reacts with dilute sulphuric acid:

$$\text{copper oxide} + \text{sulphuric acid} \longrightarrow \text{copper sulphate} + \text{water}$$

$$\left.\begin{array}{ll}\text{copper} & 63.6\\ \text{oxygen} & 16\end{array}\right\}79.6 \quad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\}98 \quad \left.\begin{array}{ll}\text{copper} & 63.6\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\}159.6 \quad \left.\begin{array}{ll}\text{hydrogen} & 2\\ \text{oxygen} & 16\end{array}\right\}18$$

This fact is utilized in one process of manufacture of copper sulphate.

It will be seen that the oxide method of forming a salt is closely similar to the method of neutralization. In both cases the products formed are water and a salt. This illustrates the fact that oxides of the metals behave to a certain extent like bases.

In cases in which the oxide reacts more readily than the metal, the method of obtaining salts from the oxide is much employed commercially. In some cases, compounds other than the oxide are employed, on account either of their low price or of their special adaptation to the formation of the salt desired. These will be noted in connection with the different compounds.

35. Important Salts. — *Potassium chloride* closely resembles sodium chloride in appearance and general properties. It is the only soluble potassium compound occurring in extensive deposits. The chief use of potassium chloride is as a raw material for the manufacture of other potassium compounds. The most important deposit of the salt is at Stassfurt in Germany, where potassium chloride and some other salts form a great underground bed, resembling the rock salt deposits mentioned earlier. As potassium chloride is not so widely distributed as sodium chloride, the latter is used in chemical manufactures in which a chloride is necessary and the metal is not important.

Potassium nitrate (saltpeter) is a familiar salt used in the preservation of meat and in the manufacture of gunpowder. It is sometimes called *niter.* It is usually produced commercially by treating sodium nitrate with potassium chloride:

$$\begin{array}{c}\text{sodium}\\ \text{nitrate}\end{array} + \begin{array}{c}\text{potassium}\\ \text{chloride}\end{array} \longrightarrow \begin{array}{c}\text{potassium}\\ \text{nitrate}\end{array} + \text{sodium chloride}$$

$$\left.\begin{array}{lr}\text{sodium} & 23\\ \text{nitrogen} & 14\\ \text{oxygen} & 48\end{array}\right\}85 \quad \left.\begin{array}{lr}\text{potassium} & 39\\ \text{chlorine} & 35.5\end{array}\right\}74.5 \quad \left.\begin{array}{lr}\text{potassium} & 39\\ \text{nitrogen} & 14\\ \text{oxygen} & 48\end{array}\right\}101 \quad \left.\begin{array}{lr}\text{sodium} & 23\\ \text{chlorine} & 35.5\end{array}\right\}58.5$$

The above process could not be carried on if saltpeter were not much more soluble in hot water than is salt. It is an interesting example of how some special property enables us to manufacture a valuable chemical from more abundant and less expensive materials. The *sodium nitrate* comes from Chile, where there are extensive beds, and it is called Chile saltpeter. It is extensively used as a fertilizer and in the manufacture of nitric acid.

Sodium sulphate is manufactured by the reaction between salt and sulphuric acid:

$$\begin{array}{c}\text{sodium}\\ \text{chloride}\end{array} + \begin{array}{c}\text{sulphuric}\\ \text{acid}\end{array} \longrightarrow \begin{array}{c}\text{sodium}\\ \text{sulphate}\end{array} + \text{hydrochloric acid}$$

$$\left.\begin{array}{lr}\text{sodium} & 46\\ \text{chlorine} & 71\end{array}\right\}117 \quad \left.\begin{array}{lr}\text{hydrogen} & 2\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\}98 \quad \left.\begin{array}{lr}\text{sodium} & 46\\ \text{sulphur} & 32\\ \text{oxygen} & 64\end{array}\right\}142 \quad \left.\begin{array}{lr}\text{hydrogen} & 2\\ \text{chlorine} & 71\end{array}\right\}73$$

There are two interesting things about this reaction. One is that we get two valuable substances from a single action — sodium sulphate and hydrochloric acid. The other is the double replacement that takes place: sodium replaces hydrogen in sulphuric acid, forming sodium sulphate, and hydrogen replaces sodium in sodium chloride, forming hydrochloric acid. Sodium sulphate is familiar as a medicine under the name of *Glauber's salt.* Large quantities of the crude compound are used in glass manufacture.

Magnesium sulphate (Epsom salts) occurs in considerable quantities in mineral deposits and is found in many mineral waters. It is prepared for medicinal purposes by purifying the natural compound.

Ammonium chloride is familiarly known as *sal ammoniac.* When soft coal is heated in closed retorts for the purpose of driving off the volatile matter to form illuminating gas, the base ammonium hydroxide is obtained as a by-product. When this is neutralized with hydrochloric acid, ammonium chloride is the salt formed. This is used in batteries for ringing doorbells (Fig. 14); for cleaning soldering irons, and for many purposes in chemical manufactures.

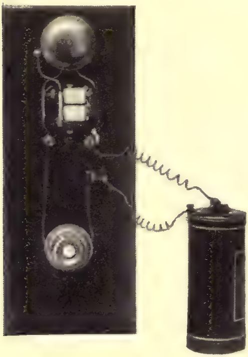


FIG. 14.

36. Salts which are not Neutral. — Many salts are not neutral like sodium chloride, but turn litmus red or blue, thus indicating the presence of an acid or a base in the solution. Thus, copper sulphate gives an acid reaction and zinc sulphate behaves in a similar manner. In these cases the salt reacts with the water in which it is dissolved, forming a very small quantity of sulphuric acid. Sodium carbonate (soda) and borax (sodium biborate), on the contrary, form basic solutions when they are dissolved in water. In each of these cases, the salt has reacted with the water, forming a small proportion of sodium hydroxide. The use of borax and soda in cleaning depends upon their alkaline properties. It is convenient to remember that salts which are formed by the reaction of an active acid with a weak or comparatively inactive base usually have an acid reaction, *e.g.* copper sulphate. The reaction of an active base with a weak acid gives such basic salts as soda and borax.

SUMMARY

IMPORTANT SALTS

COMMON NAME	CHEMICAL NAME	SOURCE	USES
Salt	Sodium chloride	Ocean, salt wells, and mines	Source of sodium and chlorine compounds. Many minor uses
——	Potassium chloride	Deposits in Germany	Source of potassium compounds
Saltpeter	Potassium nitrate	Made from sodium nitrate	Curing meat; gunpowder
Chile saltpeter	Sodium nitrate	Deposits in Chile	Fertilizer; manufacture of nitric acid
Glauber's salt	Sodium sulphate	Salt and sulphuric acid	Medicine; glass manufacture
Epsom salts	Magnesium sulphate	Natural deposits	Medicine
Sal ammoniac	Ammonium chloride	Manufacture of illuminating gas	Battery fluid
Washing soda	Sodium carbonate	Made from sodium chloride	Washing; mild alkali; glass manufacture
Borax	Sodium biborate	Borate deposits	Softening hard water
——	Zinc chloride	Zinc and hydrochloric acid	Soldering fluid
White vitriol	Zinc sulphate	Zinc and sulphuric acid	Calico printing; battery fluid
Blue vitriol	Copper sulphate	Copper and sulphuric acid	Fungicide; battery fluid

Common Salt is sodium chloride. It is obtained from natural deposits of rock salt or by the evaporation or freezing of brine.

Neutralization is the production of water and a salt by the reaction between an acid and a base.

Salts may be formed by the replacement of the hydrogen in acids by metals.

Metallic Oxides react with acids, producing water and salts.

Salts Neutral to Litmus are produced by the reaction of a strong base with a strong acid.

Salts Alkaline in Reaction are produced by the reaction of a strong base and a weak acid.

Salts Acid in Reaction are produced by the reaction of a weak base and a strong acid.

EXERCISES

1. Why are the Great Lakes not so salt as the Great Salt Lake?

2. Describe two methods of obtaining salt from solution.

3. Give five industrial uses of sodium chloride.

4. Write word equations for four cases of neutralization.

5. What will be produced if solutions of potassium hydroxide and hydrochloric acid are mixed? Solutions of sodium hydroxide and sulphuric acid?

6. Name a compound that is always formed during neutralization.

7. Why is hydrochloric acid frequently used for cleaning metals?

8. Give three ways in which magnesium chloride may be made.

9. Name two salts used in soldering. Why are they used?

10. Explain, with illustrations, how the cost of raw material, the conditions under which the reaction takes place, and the production of useful by-products determine the commercial process for producing a salt.

11. Give the chemical names of common salt; blue vitriol; saltpeter; Epsom salts; sal ammoniac; borax.

12. Would you expect copper nitrate to be neutral, acid, or alkaline in reaction? Give reason.

13. Large quantities of sodium carbonate are used in the refining of kerosene, which has previously been treated with sulphuric acid. On what property of sodium carbonate does this use depend?

14. Why are washing soda and borax used in washing clothes?

15. Explain, with an example, what is meant by double replacement.

CHAPTER VI

WEIGHT RELATIONS

37. Importance of Weight Relations. — In the development of chemistry the study of weight relations has played a very important part. It is only by comprehending these relations that we can gain certain important aids for understanding chemical ideas.

FIG. 15. — ANALYTICAL BALANCE.

To illustrate what is meant by the determination of weight relations we will consider the following experiment. A small quantity of copper is weighed in a crucible. Sulphur is added and the crucible is heated until the copper has combined with sulphur and the excess of sulphur, if any, has been driven off by heat. The crucible, which should now contain nothing but copper sulphide, is allowed to cool and is again weighed. The following data are thus obtained. Actual weights are given to serve as an example.

(*a*)	Weight of crucible + copper	7.37 g.
(*b*)	Weight of crucible	6.32 g.
(*c*)	Weight of copper	1.05 g.
(*d*)	Weight of crucible + copper sulphide	7.89 g.
(*e*)	Weight of crucible	6.32 g.
(*f*)	Weight of copper sulphide	1.57 g.
(*g*)	Weight of sulphur	0.52 g.

This experiment shows that 1.05 g. of copper requires 0.52 g. of sulphur to form copper sulphide. We may also say that the *relative* quantities of the two elements are expressed by the *ratio* 1.05 : 0.52. Notice that this ratio may be expressed with sufficient accuracy in simpler terms, since one of the numbers is almost exactly half the other. The ratio then becomes 2 : 1. If we wish we may put the ratio in still other terms, such as 4 : 2 or 20 : 10, without altering its value. This shows what we mean when we speak of relative numbers. In any particular experiment, the weights of copper and sulphur may be very large or very small, but the weight of the copper will always be twice the weight of the sulphur.

Weight relations can be found in this way for all the elements that enter into combination with each other. Early in the history of chemistry it was noticed, on comparing two weight ratios in which one of the two elements was the same, that a remarkable regularity existed.

38. Reacting Weights. — To make this regularity easily seen it is necessary to have a system for expressing the ratios. This is done by finding for each element the weight of it that combines with 16 parts of oxygen. Oxygen is chosen for the standard because most of the elements combine with it; the value is placed at 16 because this is a whole number and is large enough to avoid making the number for hydrogen, the lightest element, less than 1. We will speak of the number so found for each element as its *reacting weight.* A few of them are as follows:

Magnesium	24
Zinc	65
Mercury	200
Chlorine	71
Sulphur	16
Tin	119

Now examine the weight ratios for several compounds formed by combinations among the above elements:

Zinc sulphide, zinc 65 parts, sulphur 32 parts;

Magnesium chloride, magnesium 24 parts, chlorine 71 parts;

Mercuric chloride, mercury 200 parts, chlorine 71 parts;

Tin chloride, tin 119 parts, chlorine 142 parts.

These four ratios as found experimentally would of course give us ratios expressed in smaller numbers. In each case, the two terms of the ratio have been multiplied by such a number that the first term will be the reacting weight as given in the above table for that element. *Notice that the second number is also either the reacting weight given in the table, or a multiple of it.* This is the "remarkable regularity" referred to above, and is one of the principal reasons for the invention of the atomic hypothesis, an almost indispensable aid for the study of chemistry.

39. Law of Definite Proportions. — The facts stated in §§ 37 and 38 are embodied in two laws first stated in 1805 by John Dalton, an English chemist. He also devised the atomic hypothesis as an explanation of these laws. He first stated the very simple fact that every chemical compound always has the same elements in the same proportion by weight. The usual statement of the law is — *Every chemical compound has a definite composition by weight.* Any substance which follows this law is a chemical compound; anything that does not is a mixture.

40. Law of Multiple Proportions. — The second law deals with those cases in which two or more compounds are formed from the same elements. For example, nitrogen and oxygen form five different compounds as follows:

Compound	Nitrogen	Oxygen
Nitrous oxide	28	16
Nitric oxide	28	32
Nitrogen trioxide	28	48
Nitrogen peroxide	28	64
Nitrogen pentoxide	28	80

The nitrogen number is taken as 28 in each case; we then see that the oxygen numbers are all exact multiples of 16. The law may be stated thus: *The weight ratios for compounds formed from the same elements show a multiple relation in the quantities of one element, if the other is kept fixed.*

41. Atoms. — It will be seen from what has been stated that we may think of an element as possessing a number, or set of numbers, which expresses the parts by weight of the element which enter into chemical action. Thus oxygen (always remembering that we are making our measurements on a *comparative* or reacting weight system) enters into combination only by 16's, 32's, 48's, or some other number bearing a multiple relation to 16. Chlorine combines with (or replaces) other elements only by 35.5

parts, 71 parts, 142 parts, or some other multiple of 35.5. A similar thing is true for each of the other elements.

As a reasonable explanation of these facts and of many others which cannot be discussed here, chemists suppose that an element is composed of particles, called *atoms*, which have the following characteristics:

(*a*) They are extremely small.
(*b*) All the atoms of the same element have the same weight, which is the unit weight that enters into chemical combination.
(*c*) They do *not* divide in chemical action (this is the reason that oxygen, for example, always reacts by 16's, 32's, etc.).

42. Molecules. — It is a further part of our belief that chemical compounds, such as water, sodium hydroxide, etc., are composed of groups of atoms of different elements. Thus sodium chloride is believed to be made up of small groups, each consisting of one atom of sodium united with one atom of chlorine; water to be made up of groups, each consisting of two atoms of hydrogen united to one atom of oxygen. A single one of these groups is called a *molecule*. They are so extremely small that even a minute particle of a compound contains millions of them. *A molecule is the smallest division of a substance having the properties of the mass.*

43. Symbols of Elements. — A system of symbols is used to express in a simple way the relative weights and other facts concerning atoms and molecules. To represent an atom, we use the first letter of the name of the element, in many cases taking the Latin name; often a second letter is necessary because the names of two elements begin with the same letter. Usually the second letter taken is significant in the pronunciation of the name of the element.

O means 16 parts by weight of oxygen.

H means 1 part by weight of hydrogen.

S means 32 parts by weight of sulphur.

C means 12 parts by weight of carbon.

Cl means 35.5 parts by weight of chlorine.

Ca means 40 parts by weight of calcium.

Na (from Latin *natrium*) means 23 parts by weight of sodium.

K (from Latin *kalium*) means 39 parts by weight of potassium.

Fe (from Latin *ferrum*) means 56 parts by weight of iron.

Ag (from Latin *argentum*) means 108 parts by weight of silver.

44. Formulas of Compounds. — To represent a molecule of a compound, we write in succession the symbols of the elements composing the compound, in each case following the symbol by a subscript number to represent the particular multiple of the weight that enters into the combination. Where the multiple is one, the digit is not written but is understood. For example:

H_2O represents a molecule of water, weighing 18 parts on our relative scale, and composed of 2 parts of hydrogen (2 atoms) and 16 parts of oxygen (1 atom).

HCl represents one molecule of hydrogen chloride, weighing 36.5 parts, composed of 1 part of hydrogen (1 atom) and 35.5 parts of chlorine (1 atom).

Na_2SO_4 represents one molecule of sodium sulphate, weighing 142 parts, composed of 46 parts of sodium (2 atoms), 32 parts of sulphur (1 atom), and 64 parts of oxygen (4 atoms).

45. Atomic Weights of Important Elements. —

Aluminum	27	Iodine	127	Phosphorus	31
Barium	137	Iron	56	Platinum	195
Bromine	80	Lead	207	Potassium	39
Calcium	40	Magnesium	24	Silicon	28
Carbon	12	Manganese	55	Silver	108
Chlorine	35.5	Mercury	200	Sodium	23
Copper	63.6	Nickel	59	Sulphur	32
Gold	197	Nitrogen	14	Tin	119
Hydrogen	1	Oxygen	16	Zinc	65

46. Atomic and Molecular Weights. — The numbers given in the table (§ 45) are spoken of as *atomic weights.* They are believed to express the relative (comparative) weights of the atoms of the different elements. The standard is the weight of the oxygen atom, placed at 16, for the same reasons that governed our choice of a standard for reacting weights.

The weight of a molecule of a compound is the sum of the weight of the atoms which compose it. Molecular weights can be determined directly by experiment.

47. Formulas of Some Substances. — (*For reference only.*)

Acetic acid, $HC_2H_3O_2$
Ammonium chloride, NH_4Cl
Ammonium hydroxide, NH_4OH
Borax, $Na_2B_4O_7$
Calcium hydroxide, $Ca(OH)_2$
Calcium oxide, CaO
Carbon dioxide, CO_2
Citric acid, $H_3C_6H_5O_7$
Copper sulphate, $CuSO_4$
Copper sulphide, CuS
Hydrochloric acid, HCl
Hydrogen, H_2
Lead nitrate, $Pb(NO_3)_2$
Magnesium oxide, MgO
Magnesium sulphate, $MgSO_4$
Mercuric oxide, HgO
Nitric acid, HNO_3
Oxalic acid, $H_2C_2O_4$
Oxygen, O_2
Phosphoric acid, H_3PO_4
Phosphorus pentoxide, P_2O_5
Potassium chlorate, $KClO_3$
Potassium hydroxide, KOH
Potassium nitrate, KNO_3
Silver nitrate, $AgNO_3$
Sodium bicarbonate, $NaHCO_3$
Sodium carbonate, Na_2CO_3
Sodium chloride, $NaCl$
Sodium hydroxide, $NaOH$
Sodium sulphate, Na_2SO_4

Sulphuric acid, H_2SO_4	Water, H_2O
Tartaric acid, $H_2C_4H_4O_6$	Zinc nitrate, $Zn(NO_3)_2$
Tin oxide, SnO_2	Zinc sulphate, $ZnSO_4$

48. Equations for Some Reactions. — (*For reference only.*)

Decomposition of mercuric oxide :

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

Decomposition of water by the electric current :

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Formation of copper sulphide :

$$Cu + S \longrightarrow CuS$$

Formation of tin oxide :

$$Sn + O_2 \longrightarrow SnO_2$$

Formation of mercuric iodide :

$$Hg + I_2 \longrightarrow HgI_2$$

The burning of magnesium :

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

The burning of phosphorus :

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5$$

The burning of carbon :

$$C + O_2 \longrightarrow CO_2$$

Replacement of lead by zinc :

$$Pb(NO_3)_2 + Zn \longrightarrow Zn(NO_3)_2 + Pb$$

Replacement of hydrogen in hydrochloric acid by zinc :

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

Replacement of hydrogen in sulphuric acid by zinc :

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Action of magnesium with hydrochloric acid :

$$Mg + 2\,HCl \longrightarrow MgCl_2 + H_2$$

Action of copper oxide with sulphuric acid :

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

Action of sodium nitrate with potassium chloride :

$$NaNO_3 + KCl \rightleftarrows KNO_3 + NaCl$$

Action of sodium chloride with sulphuric acid :

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

SUMMARY

Study of the Weight Relations of chemical compounds reveals certain regularities known as the Law of Definite Proportions and the Law of Multiple Proportions.

Law of Definite Proportions: Every chemical compound has a definite composition by weight.

Law of Multiple Proportions: The weight ratios of compounds formed from the same elements show a multiple relation in the quantities of one element if the other is kept fixed.

These Laws are Explained by Atomic Theory. According to this theory, the elements are composed of particles which are: (*a*) extremely small, (*b*) of the same weight for a given element, and (*c*) indivisible in chemical action.

Molecules are the smallest divisions of a substance having the properties of the mass. They consist of one, two, or more atoms. They do not break up in physical change, but do in chemical change.

Atomic Weights are numbers that express the comparative or relative weights of the atoms of different elements. The basis of this comparative system is the weight of the atom of oxygen, 16.

Symbols are letters that stand for atoms, and hence weights of the elements. O means 1 atom of oxygen, weight 16; N means 1 atom of nitrogen, weight 14.

Formulas used to represent molecules, and hence weights of substances, are aggregations of symbols followed by numerals, expressed or understood. They indicate the composition of the substance. H_2O stands for 18 parts by weight of water, and indicates that the substance is composed of 2 parts of hydrogen and 16 parts of oxygen.

A Molecular Weight is the sum of the weights of the atoms that make up a molecule of a substance.

EXERCISES

1. What is meant by the term *relative quantities?* Illustrate. What is meant by the term *ratio?* Illustrate.

2. How would you determine the reacting weight of magnesium?

3. What uniformity or regularity is observed by inspecting the reacting weights of different elements?

4. What is meant by saying that oxygen enters into combination only by 16's? Chlorine by 35.5's?

5. According to the atomic theory, what characteristics have atoms?

6. What is the atomic weight of an element? What is the atomic weight of oxygen? Explain why this number is chosen as a standard.

7. What are molecules?

8. Give symbols for the elements sulphur, magnesium, iron, sodium, chlorine, potassium. What does the symbol mean in each case? What are molecular weights?

9. What is the formula for water? What does it mean? What is the formula for sodium sulphate? What does it mean?

10. A molecule of magnesium chloride consists of one atom of magnesium and two atoms of chlorine. Write a formula for the substance. What is the weight composition of magnesium chloride?

11. A molecule of iron (ferrous) sulphate consists of one atom of iron, one atom of sulphur, and four atoms of oxygen. What is its formula? What is its weight composition?

12. State the Law of Definite Proportions.

13. State the Law of Multiple Proportions.

14. The weight composition of hydrogen peroxide is 32 parts of oxygen to 2 parts of hydrogen. Show how the composition of this compound and the composition of water illustrate the law of multiple proportions.

15. Calculate the molecular weight of sulphuric acid, H_2SO_4.

16. Write the equations given in § 48, placing the name of each substance beneath its formula.

Note to Instructor. — The equations in § 48 were given for reference only. Until he has studied Chapters VII and VIII, the student is not expected to do anything more with them than is required by this Exercise 16.

CHAPTER VII

NOMENCLATURE AND VALENCE

A NUMBER of examples of simple equations have been given. The writing of chemical equations requires a knowledge of the chemical changes involved, an acquaintance with nomenclature, and the remembrance of valence. The rules for the naming of inorganic acids, bases, and salts are simple and can be learned with little difficulty.

49. Binary Compounds are those that contain two elements. Sometimes a group of elements plays the rôle of the positive element. Binary compounds have names ending in **-ide**. The ending -ide is added to a root derived from the name of the negative element (§ 51) entering the molecule. Binary compounds containing oxygen are oxides, those containing chlorine are chlorides, those containing sulphur are sulphides, etc. This rule does not apply to compounds of carbon and hydrogen, on account of the large number of such substances known.

50. Valence is the term used to designate the combining power of one atom of an element, or that of a group of atoms acting like an element, compared with the combining power of the hydrogen atom. If one atom of an element will combine with one atom of hydrogen, or if one atom of an element can replace one atom of hydrogen in a compound, the element is said to have a valence of one.

51. Positive and Negative Elements. — The element is negative if, on the electrolysis of the compound, it is attracted to the positive electrode (anode), and positive if it is attracted to the negative electrode (cathode). In general, elements that combine with hydrogen are negative, while those that replace hydrogen are positive. Usually positive elements are metals and negative elements are non-metals. Chlorine, bromine, and iodine are common negative elements having a valence of one. In addition to these, it is convenient to consider the hydroxyl group, OH, as being a negative group having a valence of one. Thus we have the compounds

hydrogen chloride, HCl,
hydrogen bromide, HBr,
hydrogen iodide, HI,

and water, which might be called

hydrogen hydroxide, HOH.

The same element may have more than one valence.

52. Important Valences. — The common positive elements having a valence of one are sodium, potassium, copper in cuprous compounds, silver, and mercury in mercurous compounds. In connection with these, the student should remember the group NH_4, called the ammonium group. Thus, corresponding to hydrogen chloride, we have

ammonium chloride, NH_4Cl,
sodium chloride, NaCl,
potassium chloride, KCl,

cuprous chloride, CuCl,
silver chloride, AgCl,
mercurous chloride, HgCl.

Sulphur and oxygen combine with two atoms of hydrogen. They, consequently, have a valence of two and are negative elements:

hydrogen sulphide, H_2S,
water, H_2O.

One atom of each of the elements magnesium, calcium, zinc, and barium will take the place of two atoms of hydrogen. They are positive elements having a valence of two. Binary compounds in which iron and tin have a valence of two are termed respectively ferrous compounds and stannous compounds; those in which copper and mercury have a valence of two are termed respectively cupric compounds and mercuric compounds. It will be noticed that the ending **-ous** refers to the **less** and the ending **-ic** to the **greater** valence of the **positive** element. The chlorine compounds of the elements just mentioned may be taken as illustrations of compounds of positive elements having a valence of two:

magnesium chloride, $MgCl_2$,
calcium chloride, $CaCl_2$,
ferrous chloride, $FeCl_2$,
cupric chloride, $CuCl_2$,
zinc chloride, $ZnCl_2$,
stannous chloride, $SnCl_2$,
barium chloride, $BaCl_2$,
mercuric chloride, $HgCl_2$.

The elements aluminum, chromium, and iron (in ferric compounds) are positive in most of the compounds the beginner is likely to meet, and have a valence of three. Thus we have the compounds

$AlCl_3$, aluminum chloride,
$CrCl_3$, chromium chloride,
$FeCl_3$, ferric chloride.

Carbon, silicon, and tin (in stannic compounds) have a valence of four. The only important exception to this is carbon monoxide, CO, in which the valence of carbon is two.

CCl_4, carbon tetrachloride,
$SiCl_4$, silicon tetrachloride,
$SnCl_4$, stannic chloride.

The elements nitrogen, phosphorus, arsenic, antimony, and bismuth commonly have a valence of either three or five.

53. Prefixes indicating Number of Atoms. — The terms **mono-** (one), **di-** (two), **tri-** (three), **tetra-** (four), and **penta-** (five) are frequently used to indicate the number of atoms of the element before whose name the prefix is placed. For example,

CO is carbon monoxide,	P_2O_3, phosphorus trioxide,
CO_2, carbon dioxide,	P_2O_5, phosphorus pentoxide,

CCl_4, carbon tetrachloride.

54. Satisfaction of Valences. — In a molecule there are as many positive valences as there are negative valences. One atom of a positive element having a valence of one can unite with one atom of a negative element having the same valence, while two atoms of a positive element having a valence of one would be required to combine with one atom of a negative element having a valence of two. Three atoms of a positive element having a valence of two would be required to combine with two atoms of a negative element having a valence of three, and so on.

The valences given are the common ones the beginner is likely to meet. As he advances, he will learn of cases where the elements have other valences than those given in this chapter, but by that time he is likely to be so familiar with formulas that the new valences will cause little trouble.

55. Electrochemical Series. — The terms *positive* and *negative* applied to elements are relative. It is possible to arrange the elements so that each is positive to any element placed above it and negative to any element placed below it. The following shows the more common elements thus arranged:

Negative end.
Oxygen
Sulphur
Nitrogen
Chlorine
Bromine
Iodine
Phosphorus
Arsenic
Chromium
Boron
Carbon
Antimony
Silicon
Tin
Hydrogen
Gold
Platinum
Mercury
Silver
Copper
Bismuth
Lead
Nickel
Iron
Zinc
Manganese
Aluminum
Magnesium
Calcium
Strontium
Barium
Sodium
Potassium
Positive end.

56. Bases. — A base is the hydroxide of a metal, or the hydroxide of a group of atoms playing the rôle of a metal. The common bases are

ammonium hydroxide, NH_4OH,
sodium hydroxide, $NaOH$,
potassium hydroxide, KOH,
calcium hydroxide, $Ca(OH)_2$.

57. Nomenclature of Acids. — The formulas for simple acids and salts, and the names of the corresponding compounds, may be readily mastered if the student will take time to commit to memory the names and formulas of a few *acids which contain oxygen and have names ending in -ic.* These acids and formulas are —

nitric acid, HNO_3,
chloric acid, $HClO_3$,
sulphuric acid, H_2SO_4,
phosphoric acid, H_3PO_4,
carbonic acid, H_2CO_3.

The names are formed by adding **-ic** to a root derived from the characteristic negative element contained in the acid. This root may be the entire name of the negative element, as in the case of the sulphur acids; or it may be a part of the name of the negative element, as in the case of the acids of chlorine, where chlor- is the root. Having committed to memory the name and formula for the **-ic** acid, the names and formulas for other acids of any series may be obtained by application of the following rules:

An *acid containing one less atom of oxygen than the -ic acid* has its name formed by the addition of **-ous** to the root. $HClO_2$ is chlorous acid; H_2SO_3, sulphurous acid.

If the *acid contains less oxygen than the -ous acid*, its name is formed by prefixing **hypo-** to the name of the -ous acid. HClO is the formula for **hypo**chlorous acid.

An *acid containing more oxygen than the -ic acid* has its name formed by prefixing **per-** to the name of the -ic acid. $HClO_4$ is the formula for **per**chloric acid.

When the *acid contains no oxygen*, its name is formed by prefixing **hydro-** to the name of the -ic acid. HCl is the formula for **hydro**chloric acid.

58. Nomenclature of Salts. — Normal salts are those in which all of the replaceable hydrogen of an acid has been exchanged for a metal. When an acid contains oxygen and has a name ending in **-ic**, salts of that acid end in **-ate.** If the acid ends in **-ous,** salts of that acid end in **-ite.** Salts of **hypo-** ··· **-ous** acids end in **-ite.** The names of the sodium compounds illustrating these rules are given in the Summary under the heading of Salts (page 64).

59. Acid Radical. — An acid radical is the acid minus its replaceable hydrogen; that is, the radical for sulphuric acid is $-SO_4$ and that of carbonic acid is $-CO_3$. In case only a part of the hydrogen which the acid contains can be exchanged for a metal, the replaceable hydrogen should be indicated in the formula. For example, the formula for tartaric acid is written $H_2(C_4H_4O_6)$ to show that two of the six hydrogen atoms which the molecule contains can be replaced by a metal, and that the remaining four hydrogen atoms form a part of the acid radical. Since each hydrogen atom has a valence of one, the acid radical has a valence equal to the number of hydrogen atoms with which it unites.

As soon as the student has learned the valences of the metals, the formulas for the -ic acids, and the rules for naming acids and salts, the writing of the formula for any common salt becomes simple. The molecule is electrically neutral. It may be looked upon as formed by the combination of one part, carrying a definite number of positive charges, with another part, carrying an equal number of negative charges. For example, consider the sodium salt of nitric acid. The formula for nitric acid is HNO_3. Evidently the acid radical $-NO_3$ has a valence of one and makes up the negative part of the molecule. The valence of potassium is one, and potassium is a positive element. The K^+ would unite with the NO_3^- to form KNO_3. Since the salt is derived from an acid containing oxygen and having a name ending in -ic, the salt would have a name ending in -ate, that is, it is a nitrate. The metal contained in the salt is potassium, therefore the salt is a potassium salt and the full name of it is potassium nitrate.

Mercury in mercuric compounds has a valence of two (Hg^{++}). It is evident from what has already been said that two NO_3^- groups would unite with one Hg^{++} group and that the formula for mercuric nitrate would be $Hg(NO_3)_2$. The normal salt derived from Ca^{++} and H_3PO_4 would be calcium phosphate, $Ca_3(PO_4)_2$. The formula for potassium tartrate would be $K_2(C_4H_4O_6)$ and that of sodium carbonate is Na_2CO_3.

60. Acid and Basic Salts. — In addition to normal salts, formed by exchanging all the replaceable hydrogen of an acid for a metal, acid and basic salts are known. An *acid salt* is formed when only a part of the replaceable hydrogen of an acid molecule is exchanged for a metal. Thus we have $KHSO_4$, potassium acid sulphate, and

$KH(C_4H_4O_6)$, as illustrations of an acid salt of sulphuric acid and tartaric acid respectively.

A *basic salt* is formed when only a part of the hydroxyl (OH) of a base is exchanged for an acid radical. Thus from the base bismuth hydroxide, $Bi(OH)_3$, and nitric acid we may have basic bismuth nitrate, $Bi(OH)_2NO_3$.

SUMMARY

A Radical is a group of elements which tend to cling together during a chemical change. Radicals generally remain unaltered during chemical reactions.

Valence is the combining power of 1 atom of an element or the combining power of a radical, compared with the combining power of 1 atom of hydrogen.

Positive and Negative Elements. — Bodies charged with opposite kinds of electricity attract each other. Positive elements and radicals are those which, on the electrolysis of their compounds, appear at the negative electrode (cathode). The terms positive and negative are relative. The elements may be arranged in an electrochemical series (page 59) so that each of the elements will be positive to all elements above it, and negative to all appearing in the table below it. The following table of valences is likely to be of service to the beginner:

+	+ +	+ + +
HYDROGEN	MAGNESIUM	ALUMINUM
AMMONIUM (NH_4)	CALCIUM	CHROMIUM
SODIUM	IRON (in ferrous compounds)	IRON (in ferric compounds)
POTASSIUM	COPPER (in cupric compounds)	
COPPER (in cuprous compounds)	ZINC	
SILVER	BARIUM	
MERCURY (in mercurous compounds)	MERCURY (in mercuric compounds)	

—	— —	— — — —
HYDROXYL (OH)	OXYGEN	CARBON
FLUORINE	SULPHUR	SILICON
CHLORINE		
BROMINE		
IODINE		

RULES FOR NAMING INORGANIC COMPOUNDS

Binary Compounds. — The name of an inorganic compound consists of two parts. The first part is either the name of the positive element or is derived from it. The ending *-ous* applied to the first part of the name indicates that the valence of the positive element is less than it is when the ending *-ic* is used. In binary compounds, the second part is formed by adding *-ide* to a root derived from the name of the negative element. The prefixes *mono-, di-, tri-, tetra-,* etc. are often used to indicate the number of negative atoms in the molecule.

A Base is the hydroxide of a metal or of a metallic radical. The name of a base consists of the name of the metallic element or radical followed by the word *hydroxide*.

Acids. — The rules for naming the acids belonging to the same series may be indicated as follows:

Hydrochlor**ic** acid	HCl	Molecule contains no oxygen
Hypochlor**ous** acid	$HClO$	1 less atom of oxygen than chlor**ous** acid
Chlor**ous** acid	$HClO_2$	1 less atom of oxygen than chlor**ic** acid
Chlor**ic** acid	$HClO_3$	STARTING POINT
Perchlor**ic**	$HClO_4$	1 more atom of oxygen than chlor**ic** acid

Salts. — An acid radical may be regarded as an acid minus its replaceable hydrogen. An acid and its salts contain the same radical. Salts of acids that contain oxygen and have names ending in -**ic** are given names ending in -**ate.** Salts of acids ending in -**ous** have names ending in -**ite**. Salts of acids that contain no oxygen have names ending in **-ide.** They follow the rules for binary compounds.

Acid		Sodium Salt	
Hydrochlor**ic** acid	HCl	Sodium chlor**ide**	$NaCl$
Hypochlor**ous** acid	$HClO$	Sodium **hypo**chlor**ite**	$NaClO$
Chlor**ous** acid	$HClO_2$	Sodium chlor**ite**	$NaClO_2$
Chlor**ic** acid	$HClO_3$	Sodium chlor**ate**	$NaClO_3$
Perchlor**ic** acid	$HClO_4$	Sodium **per**chlor**ate**	$NaClO_4$

EXERCISES

1. Of what value is a knowledge of valence and the rules of nomenclature?

2. What is a binary compound?

3. Give the general rules for naming binary compounds.

4. Define valence.

5. The valence of magnesium is 2. Write the formula for magnesium oxide.

6. Aluminum has a valence of 3. What is the formula for aluminum oxide?

7. Give the chemical names of the compounds represented by the following formulas: H_2O, H_2O_2, $NaCl$, $CaCl_2$, FeO, Fe_2O_3, CCl_4, CO, CO_2, MnO_2.

8. Write the formulas for the following compounds: potassium bromide, zinc sulphide, cuprous oxide, cupric oxide, ferrous chloride, ferric chloride, ferric sulphate, aluminum sulphate, ammonium sulphide, aluminum hydroxide.

9. What is a base? Give the names and formulas of five bases.

10. Write the formulas of the following: chloric acid, nitric acid, sulphuric acid, carbonic acid, phosphoric acid.

11. State the general rules for naming acids.

12. Why is it unnecessary to commit to memory the valence of an acid radical?

13. What are the formulas for the following: nitrous acid, hypophosphorous acid, sulphurous acid, hydrosulphuric acid, perchloric acid?

14. How does the formula for a salt differ from that of the corresponding acid?

15. Give the general rules for naming salts.

16. $PbCrO_4$ is the formula for lead chromate. What is the formula for chromic acid? What is the valence of the radical CrO_4?

17. $NaIO_4$ is the formula for sodium periodate. What is the formula for iodic acid?

18. What is the formula for calcium hypochlorite?

19. The formula for acetic acid is sometimes written $H(C_2H_3O_2)$ to show that one molecule of the acid contains one atom of replaceable hydrogen, and that the acid radical is $C_2H_3O_2$. What is the formula for lead acetate?

20. The formula for tartaric acid is $H_2(C_4H_4O_6)$. What is the formula for potassium hydrogen tartrate?

CHAPTER VIII

THE WRITING OF CHEMICAL EQUATIONS

61. Basis of Chemical Equations. — It is difficult to get the beginner to realize that true chemical equations are based on results actually obtained in the laboratory. After a large number of cases have been examined, certain principles governing chemical reactions may be discovered, but the factors which enter the reaction may be so many that it is impossible for the inexperienced student to predict with certainty what change will take place. Before any chemical equation can be correctly written, the chemical change that actually takes place must be known. The chemical changes commonly met with in elementary chemistry are direct decomposition, direct combination, simple replacement, and double replacement.

62. Direct Decomposition is the separation of one compound into two or more substances. Two illustrations of this class of chemical change are the decomposition of water by electrolysis and the separation of mercuric oxide, when heated, into mercury and oxygen. Let us consider the writing of the equations used to represent these changes.

The student is supposed to know that the valence of mercury in mercuric compounds is 2, that the valence of oxygen is 2, and that, therefore, the formula for mercuric oxide is HgO. He has seen that mercuric oxide, on being heated, decomposes into mercury and oxygen. He is therefore at liberty to write the chemical equation representing the change: $HgO \longrightarrow Hg + O$. But chemists recognize three kinds of oxygen; nascent oxygen, ordinary oxygen, and ozone. *Nascent oxygen* is considered to be atomic oxygen (oxygen as it occurs at the instant it is liberated from a chemical compound). *Ordinary oxygen* is believed to be composed of molecules each of which contains 2 atoms. *Ozone* is thought to be made of molecules each containing 3 atoms of oxygen. Now, the oxygen that the student obtained when he decomposed mercuric oxide was ordinary oxygen. To show this fact, O_2 should take the place of O in the equation. As the number of atoms of mercury in a molecule of liquid mercury is not known, the simplest number is assumed to be correct, so Hg is used to represent a molecule as well as an atom of mercury. The equation would then become $HgO \longrightarrow Hg + O_2$. But this is not a true equation because it represents the creation of an additional atom of oxygen, or in other words, the equation is not balanced. As the composition of the molecules cannot be changed without changing the kinds of matter to be represented, the number of molecules must be made such that the number of atoms of any element on one side of the equation will equal the number of atoms of that element on the other side of the equation. This is accomplished by the use of coefficients and the equation is made to read:

$$\underset{\text{mercury oxide}}{2\,HgO} \longrightarrow \underset{\text{mercury}}{2\,Hg} + \underset{\text{oxygen}}{O_2}$$

In writing the equation representing the decomposition of water, the formula for a molecule of water, and the formulas for molecules of the products may first be written $H_2O \longrightarrow H_2 + O_2$, and the equation then balanced by the use of the right coefficients:

$$\underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{hydrogen}}{2\,H_2} + \underset{\text{oxygen}}{O_2}$$

Molecules of the elementary gases hydrogen, chlorine, oxygen, and nitrogen each contain two atoms. Phosphorus and arsenic in gaseous form are composed of molecules containing four atoms each. The formulas for molecules of these elements are sometimes written P_4 and As_4. Some elements in the form of a gas, for example, mercury and sodium, are made up of molecules each having a mass equal to that of the atom (Hg and Na).

Sometimes chemical decomposition takes place, during which one compound is made to yield two compounds. For example, all common carbonates, with the exception of those of sodium and potassium, when heated break up before they melt, yielding carbon dioxide and a metallic oxide. Thus calcium carbonate, when heated to a high temperature, yields carbon dioxide and calcium oxide:

$$\underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2} + \underset{\substack{\text{calcium}\\ \text{oxide}}}{CaO}$$

63. Direct Combination. — Equations representing cases of direct combination usually involve the chemical union of two elements, but also include the union of molecules of two compounds. A few examples may make clear the meaning of this statement. Oxygen having a valence of 2, enters into direct combination with carbon, having a valence of 4, to form carbon dioxide:

$$\underset{\text{carbon}}{C} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2}$$

Copper unites with sulphur to form copper sulphide:

$$\underset{\text{copper}}{Cu} + \underset{\text{sulphur}}{S} \longrightarrow \underset{\substack{\text{copper}\\ \text{sulphide}}}{CuS}$$

Molecules of copper sulphate enter into direct combination with molecules of water to form crystallized copper sulphate:

$$\underset{\substack{\text{copper}\\\text{sulphate}}}{CuSO_4} + \underset{\text{water}}{5\,H_2O} \longrightarrow \underset{\substack{\text{crystallized}\\\text{copper sulphate}}}{CuSO_4 \cdot 5\,H_2O}$$

Frequently an *acid anhydride* (an acid minus water) when fused with a *basic anhydride* (a base minus water) will combine to form a salt. For example, calcium silicate may be obtained by fusing together calcium oxide (the anhydride of calcium hydroxide) and silicon dioxide (the anhydride of silicic acid):

$$\underset{\substack{\text{calcium}\\\text{oxide}}}{CaO} + \underset{\substack{\text{silicon}\\\text{dioxide}}}{SiO_2} \longrightarrow \underset{\substack{\text{calcium}\\\text{silicate}}}{CaSiO_3}$$

64. Simple Replacement. — Cases of simple replacement are frequently met with in the laboratory. The replacement of the hydrogen of an acid by a metal, the decomposition of water by a metal, the replacement of a combined metal by a free metal, and the replacement of one non-metallic element by another non-metallic element come under this head.

The atom of zinc has a valence of 2. A molecule of hydrochloric acid contains one atom of replaceable hydrogen. Therefore 1 atom of zinc, when it reacts with hydrochloric acid, takes the place of the hydrogen in 2 molecules of hydrochloric acid:

$$\underset{\text{zinc}}{Zn} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{2\,HCl} \longrightarrow \underset{\substack{\text{zinc}\\\text{chloride}}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2}$$

The student should remember that every metal cannot directly replace the hydrogen of every acid. In many instances, the acid does not react with the metal, and in many other cases, a secondary reaction takes place, during which some of the acid molecules lose oxygen, which converts the replaced hydrogen into water.

Other illustrations of simple replacement are represented by the equations:

$$\underset{\text{sodium}}{2\,\mathrm{Na}} + \underset{\text{water}}{2\,\mathrm{HOH}} \longrightarrow \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{2\,\mathrm{NaOH}} + \underset{\text{hydrogen}}{\mathrm{H_2}}$$

$$\underset{\substack{\text{silver}\\ \text{sulphate}}}{\mathrm{Ag_2SO_4}} + \underset{\text{copper}}{\mathrm{Cu}} \longrightarrow \underset{\substack{\text{copper}\\ \text{sulphate}}}{\mathrm{CuSO_4}} + \underset{\text{silver}}{2\,\mathrm{Ag}}$$

$$\underset{\substack{\text{potassium}\\ \text{bromide}}}{2\,\mathrm{KBr}} + \underset{\text{chlorine}}{\mathrm{Cl_2}} \longrightarrow \underset{\substack{\text{potassium}\\ \text{chloride}}}{2\,\mathrm{KCl}} + \underset{\text{bromine}}{\mathrm{Br_2}}$$

65. Double Replacement is the reaction of most common occurrence in chemistry. During double replacement, the positive part of one molecule exchanges place with the positive part of another molecule. This exchange of place is due to the formation of water (cases of neutralization); of a gaseous compound, or a compound which will decompose under the conditions of the experiment so as to yield a gas; or of an insoluble compound.

In cases of neutralization, the positive hydrogen of the acid combines with the negative hydroxyl of the base to form water. The components of a salt are left in solution, and the salt generally separates on evaporation of the liquid. For complete neutralization, there must be present for every acid hydrogen atom a basic hydroxyl radical.

$$\underset{\substack{\text{hydrochloric}\\ \text{acid}}}{\mathrm{HCl}} + \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{\mathrm{NaOH}} \longrightarrow \underset{\text{water}}{\mathrm{HOH}} + \underset{\substack{\text{sodium}\\ \text{chloride}}}{\mathrm{NaCl}}$$

$$\underset{\substack{\text{sulphuric}\\ \text{acid}}}{\mathrm{H_2SO_4}} + \underset{\substack{\text{potassium}\\ \text{hydroxide}}}{2\,\mathrm{KOH}} \longrightarrow \underset{\text{water}}{2\,\mathrm{HOH}} + \underset{\substack{\text{potassium}\\ \text{sulphate}}}{\mathrm{K_2SO_4}}$$

In the last equation, since every sulphuric acid molecule contains two acid hydrogen atoms, two molecules of potassium hydroxide must be taken in order to furnish the necessary number of hydroxyl groups. The following equations represent other instances of neutralization:

$$\underset{\substack{\text{calcium}\\\text{hydroxide}}}{Ca(OH)_2} + \underset{\substack{\text{nitric}\\\text{acid}}}{2\,HNO_3} \longrightarrow \underset{\text{water}}{2\,HOH} + \underset{\substack{\text{calcium}\\\text{nitrate}}}{Ca(NO_3)_2}$$

$$\underset{\substack{\text{aluminum}\\\text{hydroxide}}}{2\,Al(OH)_3} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{3\,H_2SO_4} \longrightarrow \underset{\text{water}}{6\,HOH} + \underset{\substack{\text{aluminum}\\\text{sulphate}}}{Al_2(SO_4)_3}$$

Instances in which double replacement is due to the formation of a gaseous compound may be illustrated by the reaction between sulphuric acid and the salt of an acid having a lower boiling point. When sulphuric acid is added to potassium nitrate for the purpose of making nitric acid, the temperature is so regulated that it will be a little above the boiling point of nitric acid and far below that of sulphuric acid. Under these conditions, the nitric acid as soon as it is formed escapes as a gas from the reacting mass:

$$\underset{\substack{\text{sodium}\\\text{nitrate}}}{2\,NaNO_3} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{nitric}\\\text{acid}}}{2\,HNO_3} + \underset{\substack{\text{sodium}\\\text{sulphate}}}{Na_2SO_4}$$

Ammonium hydroxide, carbonic acid, and sulphurous acid are examples of compounds that readily decompose, yielding a gas as one of the products of decomposition. When nitric acid is added to calcium carbonate, the carbonic acid formed at once decomposes into water and the gas carbon dioxide:

$$\underset{\substack{\text{calcium}\\ \text{carbonate}}}{\mathrm{CaCO_3}} + \underset{\substack{\text{nitric}\\ \text{acid}}}{2\,\mathrm{HNO_3}} \longrightarrow \underset{\substack{\text{calcium}\\ \text{nitrate}}}{\mathrm{Ca(NO_3)_2}} + \underset{\substack{\text{carbonic}\\ \text{acid}}}{\mathrm{H_2CO_3}}$$

$$\underset{\substack{\text{carbonic}\\ \text{acid}}}{\mathrm{H_2CO_3}} \longrightarrow \underset{\text{water}}{\mathrm{H_2O}} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{\mathrm{CO_2}}$$

These two equations are usually combined into one:

$$\underset{\substack{\text{calcium}\\ \text{carbonate}}}{\mathrm{CaCO_3}} + \underset{\substack{\text{nitric}\\ \text{acid}}}{2\,\mathrm{HNO_3}} \longrightarrow \underset{\substack{\text{calcium}\\ \text{nitrate}}}{\mathrm{Ca(NO_3)_2}} + \underset{\text{water}}{\mathrm{H_2O}} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{\mathrm{CO_2}}$$

In a similar manner, when an ammonium salt is heated with a non-volatile base, double replacement takes place, because as soon as the ammonium hydroxide is formed, it decomposes, yielding the gas ammonia, and water:

$$\underset{\substack{\text{ammonium}\\ \text{chloride}}}{2\,\mathrm{NH_4Cl}} + \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{\mathrm{Ca(OH)_2}} \longrightarrow \underset{\substack{\text{calcium}\\ \text{chloride}}}{\mathrm{CaCl_2}} + \underset{\substack{\text{ammonium}\\ \text{hydroxide}}}{2\,\mathrm{NH_4OH}}$$

$$\underset{\substack{\text{ammonium}\\ \text{hydroxide}}}{2\,\mathrm{NH_4OH}} \longrightarrow \underset{\text{ammonia}}{2\,\mathrm{NH_3}} + \underset{\text{water}}{2\,\mathrm{H_2O}}$$

The final equation, representing the completed reaction, is:

$$\underset{\substack{\text{ammonium}\\ \text{chloride}}}{2\,\mathrm{NH_4Cl}} + \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{\mathrm{Ca(OH)_2}} \longrightarrow \underset{\substack{\text{calcium}\\ \text{chloride}}}{\mathrm{CaCl_2}} + \underset{\text{ammonia}}{2\,\mathrm{NH_3}} + \underset{\text{water}}{2\,\mathrm{H_2O}}$$

Instances in which double replacement is due to the formation of an insoluble compound are very common; in fact, a large portion of the reactions used in analytical chemistry are double replacements. The formation of insoluble silver chloride, on the addition of a solution of silver nitrate to a solution of a soluble chloride, and the formation of insoluble barium sulphate, on the addition of a solution of barium chloride to a solution of a sulphate, are common examples:

$$\underset{\substack{\text{sodium}\\\text{chloride}}}{\mathrm{NaCl}} + \underset{\substack{\text{silver}\\\text{nitrate}}}{\mathrm{AgNO_3}} \longrightarrow \underset{\substack{\text{silver}\\\text{chloride}}}{\mathrm{AgCl}} + \underset{\substack{\text{sodium}\\\text{nitrate}}}{\mathrm{NaNO_3}}$$

$$\underset{\substack{\text{sodium}\\\text{sulphate}}}{\mathrm{Na_2SO_4}} + \underset{\substack{\text{barium}\\\text{chloride}}}{\mathrm{BaCl_2}} \longrightarrow \underset{\substack{\text{barium}\\\text{sulphate}}}{\mathrm{BaSO_4}} + \underset{\substack{\text{sodium}\\\text{chloride}}}{2\,\mathrm{NaCl}}$$

SUMMARY

Direct Decomposition is the breaking of a compound into two or more substances by the application of some form of energy.

Direct Combination is the formation of one compound from two or more substances.

Simple Replacement is the exchange of place between a combined and a free element.

Double Replacement is the exchange of place between the positive part of one molecule and the positive part of another molecule. Double replacement is generally due to one of the following:

(*a*) neutralization,
(*b*) formation of a volatile compound,
(*c*) formation of an insoluble compound.

The Writing of Chemical Formulas involves a knowledge of the symbols and the valences of the elements, and an understanding of the rules of nomenclature.

Chemical Equations are based upon data obtained in the laboratory. Before a true chemical equation can be written, the chemical change, or changes, that actually take place must be known. This implies a knowledge of the composition of the initial substances and of the products formed. The student must also understand how to use coefficients, so that the same weight of matter will be represented by each side of the equation.

EXERCISES

1. What must be known before a true chemical equation can be written?

2. What are the steps to be followed in writing a chemical equation?

3. What is the meaning of the term "direct decomposition"?

4. Mention two cases of direct decomposition that you have studied, and write the chemical equations representing them.

5. Why should ordinary oxygen be represented by the formula O_2 and not by the symbol O?

6. Magnesium carbonate, on being heated, yields carbon dioxide and magnesium oxide. Write the chemical equation representing this change.

7. Define direct combination.

8. Mention five illustrations of direct combination, and write chemical equations to represent the changes taking place.

9. What is an acid anhydride? A basic anhydride?

10. What kind of a compound is formed when an acid anhydride combines with a basic anhydride?

11. What is the meaning of the formula $CuSO_4 . 5\,H_2O$?

12. What is meant by "simple replacement"?

13. When a needle is placed in a solution of copper sulphate, it becomes coated with copper. Represent by an equation the chemical change that takes place.

14. Define "double replacement."

15. Name three conditions permitting double replacement to proceed.

16. Write the equation for the neutralization of ammonium hydroxide by sulphuric acid.

17. Silver chloride is insoluble in water. Silver nitrate is soluble. What chemical reaction occurs when a solution of sodium chloride is added to a solution of silver nitrate? Equation?

18. Hydrogen chloride is a gas. Sulphuric acid boils at 338° C. Sodium sulphate is a solid. What would be the result of heating sodium chloride with sulphuric acid? Equation?

19. Ammonium hydroxide is unstable and readily decomposes, yielding water and the gas ammonia (NH_3). What gas would be formed when an ammonium salt was treated with a non-volatile base?

20. Write the equation for the reaction between ammonium sulphate and calcium hydroxide.

NOTE TO INSTRUCTORS. — Instructors who may wish, after finishing this chapter, to give some work on chemical calculations will find ample material in Chapter XLVI, and may select the types of calculations desirable for their classes. The authors, however, believe that the greater number of instructors will take up directly the chapters immediately following this, which deal with more practical affairs of life.

CHAPTER IX

SOLUTIONS

66. Nature of Solutions. — When a spoonful of common salt is placed in a tumbler of water, the salt gradually disappears. The result is a clear, transparent liquid, any portion of which has a salty taste. Not only has the salt gone into the water, but it has penetrated every portion of it. Just how the process occurs is beyond the power of our eyes to see. We know, however, that the finer the salt is powdered, the quicker it will go into the water or dissolve. These facts lead us to think that extremely fine particles separate from the grains of salt and mix with the water particles, which are too minute to be seen. In this manner a solution of salt and water is obtained which has the remarkable property of being alike in every portion, not only as to color, transparency, and taste, but in containing the same amount of water and salt in every cubic centimeter, provided the solution has been thoroughly stirred. Thus the salt solution is a *mixture of uniform composition.*

All compounds have one property in common — uniformity of composition. Compounds are formed by elements combining in certain definite proportions by weight. At the first glance it seems as if our salt solution followed the law of definite proportions, and is therefore a chemical compound. But any compound has always the same weight composition however it is made. If we had put half a spoonful of salt into our tumbler of water, another uniform mixture of salt and water would have been obtained, but the second mixture would not have the same composition as the first. In fact many such uniform mixtures may be made by varying the relative quantities of salt and water. Hence it is seen that there is no one definite composition for salt solutions, and that any such mixture, no matter how uniform its composition may be, cannot properly be classed as a chemical compound. *A solution is a mixture of uniform composition which does not follow the law of definite proportions.*

67. Solvent and Solute. — A substance like water, which has the power of dissolving another substance, is known as a *solvent.* The substance dissolved is termed the *solute.* Although in some instances solids and gases act as solvents, liquids are the solvents of greatest practical importance. Water, alcohol, benzine, chloroform, and ether are some of the liquid solvents much employed. Although water is the solvent of common household use, other solvents are found necessary for the preparation of medicines, varnishes, and other commercial products. The most desirable solvent for a particular substance has to be determined by experiment. A knowledge of the general behavior of solvents may best be acquired by the study of water solutions.

68. Soluble and Insoluble Substances. — Sugar and salt are familiar substances that dissolve without difficulty in water, and are known therefore as substances *soluble* in water. Sand, sulphur, silver, iron, wood, and many other materials when placed in water do not dissolve. They either settle to the bottom or float on the liquid. Such substances are said to be *insoluble* in water. Hot water poured on tea leaves gives a clear yellowish liquid, showing that at least one of the substances in the tea leaves is soluble. Though the process may be repeated a large number of times, insoluble substances still remain.

The solvent action of water aids in the disintegration of rocks by taking out the soluble substances formed in processes of weathering. The value of marble, sandstone, and slate as building materials rests in part on their practical insolubility in water.

The muddy waters of brooks and rivers in spring contain substances in solution, but owe their turbidity to numberless fine particles of insoluble solids held in suspension. While a *suspension* at a given moment may have a rather uniform distribution of the solid particles, it differs from a solution in that the solid particles will separate eventually from the liquid, usually settling to the bottom. As long as the conditions affecting a solution remain unchanged, the dissolved particles remain uniformly distributed throughout the solvent.

69. Dilute and Concentrated Solutions. — Rain water always contains a very small amount of dissolved matter. Such a solution, consisting of a relatively large amount of the solvent to a small amount of the dissolved substance (solute), is a *dilute solution.* Brook and river waters are also dilute solutions, but contain a rather larger amount of dissolved matter than rain water. This additional matter is obtained from the soil. The growth and life of plants depends upon the sap, a dilute solution containing mineral substances taken in through the roots, and upon food materials made in the leaves. Most beverages contain but small amounts of the dissolved substances in large amounts of the solvent, usually water. Vinegar is mainly a very dilute solution (4 %) of acetic acid. Most medicines in liquid form are dilute solutions of various drugs.

In very dilute solutions, the particles of the dissolved substances are widely separated from each other by large quantities of the solvent. When a dilute water solution of sugar is heated, some of the water evaporates. As this process continues, some of the dissolved particles of sugar are brought closer together or concentrated in a smaller volume. In this manner, a *concentrated solution* of sugar may be obtained. Even if the dilute sugar solution was allowed to stand at the ordinary temperature, the slow evaporation of the water would give a concentrated solution. Concentrated solutions differ from dilute solutions in containing a much larger amount of dissolved substance in proportion to the amount of the solvent. Often it is more desirable to prepare a concentrated solution directly by mixing solvent and solute, rather than by evaporation of a dilute solution. Thus, caustic potash may be dissolved in its own weight of cold water ; caustic soda is more soluble. Zinc chloride, used in soldering solutions, gives still more concentrated solutions, as it dissolves in half its weight of water at ordinary temperatures. At higher temperatures, concentrated solutions of some substances may be prepared, in which a given amount of solvent contains five or six times as much of the dissolved substance.

As has been stated, the relative amounts of the solvent and the solute determine whether a solution is dilute or concentrated. When the amount of the dissolved substance is comparatively small, the solution is dilute ; when the amount of the solute is relatively large, the solution is concentrated. Like all things depending upon two variable factors, the two kinds of solution, dilute and concentrated, grade into each other. In natural processes, dilute solutions are far more common than concentrated ; in many manufacturing operations, concentrated solutions are much employed. Sometimes, however, dilute solutions are necessary. For the laboratory, concentrated solutions are the most convenient form to keep on hand. From them dilute solutions can readily be made by the addition of more of the solvent.

70. Saturated Solutions. — Experiments with dilute and concentrated solutions show that the solubility of a substance in a certain solvent has its limits. Pure salt, sodium chloride, added to cold water in small amounts slowly dissolves. Soon, however, the last portion of the salt remains undissolved, no matter how finely it may be powdered or how much the salt and water are shaken together. The given amount of water has dissolved all of the salt that it can at that temperature. Such a solution, in which the solvent at a certain temperature has dissolved all of a given substance possible, is a *saturated solution* of that substance under existing conditions. Temperature is the condition which most affects the preparation of saturated solutions.

It might be thought that the water in a saturated solution of ammonium chloride at the room temperature had reached the limit of its dissolving power at that temperature. This is true with respect to the ammonium chloride, but not with regard to other substances soluble in water. For example, magnesium sulphate will dissolve readily in such a saturated solution of ammonium chloride. Hence *a saturated solution should be defined with respect to a particular substance as well as to a definite temperature.*

Solids differ greatly in the degree of their solubility in water, hence saturated solutions of various substances at the ordinary temperature contain widely differing amounts of the dissolved substances. Limewater is a saturated solution of calcium hydroxide containing about 2 parts by weight of lime to 1000 of water. A saturated solution of boric acid contains about 4 parts in 100 of water. The ordinary sal ammoniac solution used in wet batteries, contains about 1 part of ammonium chloride to 3 parts of water.

Two other highly important conditions in the making of concentrated and saturated solutions are the size of the particles of the substance to be dissolved, and the closeness of contact of the solvent with every particle of the solute. Thus time is saved by finely powdering the solid. This is done in the laboratory with a mortar and pestle, while in manufacturing establishments grinding mills or rotary crushers are employed. In the household, stirring with a spoon brings the solvent and solute into close contact. In the laboratory, it is customary to shake the two together in a flask or test tube, or to use a stirring rod in a beaker. Technical establishments prepare large quantities of solutions in vats in which paddles are rotated.

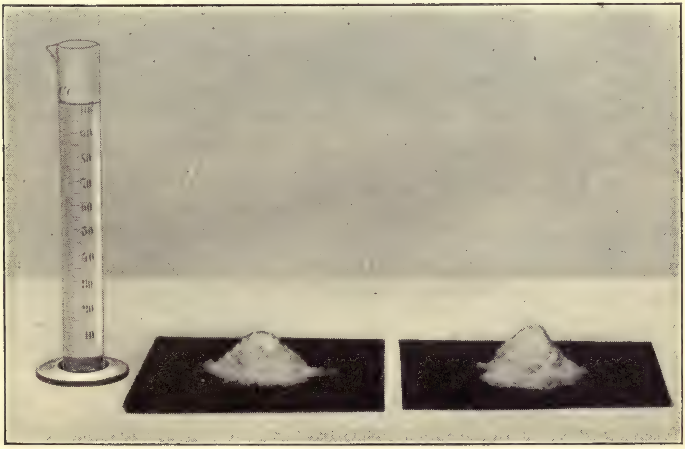


FIG. 16. — RELATIVE SOLUBILITY OF SODIUM CHLORIDE IN COLD AND IN HOT WATER.

71. Effect of Temperature on the Solubility of Solids. — When a solution of sodium chloride, which was saturated at 20° C., is heated without the loss of water to a higher temperature, it is found that a little more salt can be dissolved (Fig. 16). That is, the solution which is saturated at 20° C. is not saturated at the higher temperature. The increase in temperature has increased the solubility of sodium chloride in water. While sodium chloride is but slightly more soluble in hot water than in cold, potassium nitrate is about eight times as soluble in boiling water as in cold water (Fig. 17). Crystals of washing soda are vastly more soluble in lukewarm water (35°C.) than in water at 20° C. In general *the solubility of most solids in liquids increases with the temperature.*

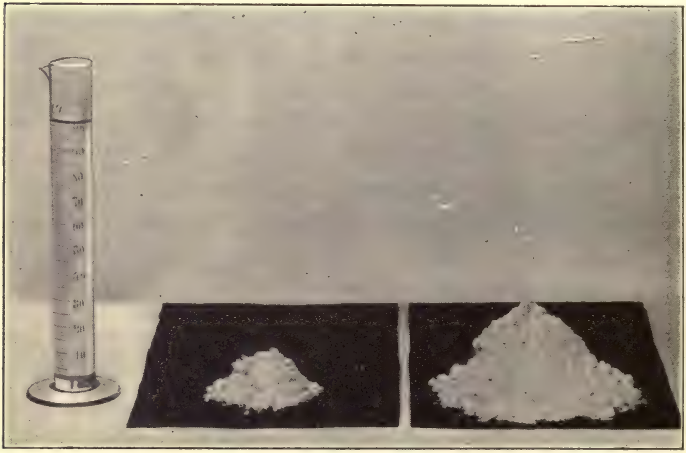


FIG. 17. — RELATIVE SOLUBILITY OF POTASSIUM NITRATE IN COLD AND IN HOT WATER.

72. Crystallization and Precipitation. — When a saturated solution of a solid is allowed to stand, the water evaporates in part. The decreased amount of the solvent means that some of the dissolved substance must come out of solution. Many of these solids in so doing deposit in crystalline form. Often the crystals are easily recognized because of their approximation to some well-known geometric form. Alum, for example, gives crystals shaped like two four-sided pyramids placed base to base, which constitute an octahedron (Fig. 18 *a*, apex of one pyramid in foreground). Sodium chloride and potassium chloride form cubical crystals similar to those in Fig. 18 *b*. Rock candy consists simply of a mass of sugar crystals whose form can easily be seen.

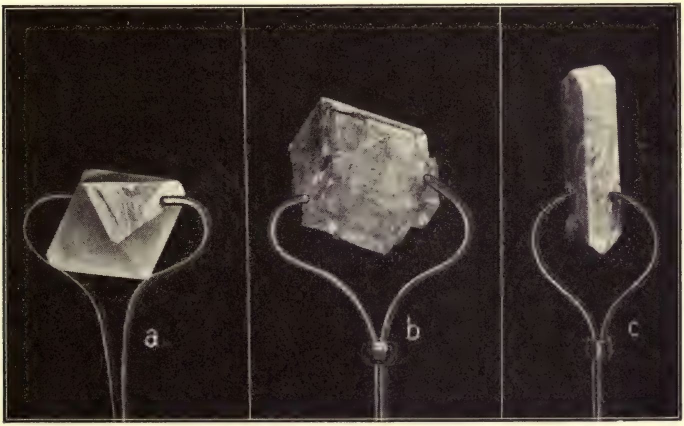


FIG. 18. — TYPICAL CRYSTALS.

a. Potassium Alum ; *b*, Sodium Nitrate ; *c*, Nickel Sulphate.

When we mix a solution of sodium chloride with a solution of silver nitrate, we obtain a white, cloudy mixture. On standing, a white solid gradually settles to the bottom of the tube. An analysis of the solid shows that it is silver chloride. This compound did not exist in either of the two solutions that we put together, but was formed on mixing them. A study of the equation for the reaction,

$$\underset{\substack{\text{sodium}\\ \text{chloride}}}{\mathrm{NaCl}} + \underset{\substack{\text{silver}\\ \text{nitrate}}}{\mathrm{AgNO_3}} \longrightarrow \underset{\substack{\text{silver}\\ \text{chloride}}}{\mathrm{AgCl}} + \underset{\substack{\text{sodium}\\ \text{nitrate}}}{\mathrm{NaNO_3}}$$

shows that it is one of double replacement. The sodium and the silver have exchanged places, forming silver chloride and sodium nitrate. The latter, being readily soluble, remains dissolved in the water of the two solutions which were mixed. Silver chloride, the other product, is only slightly soluble in water. In fact, the solution is saturated with respect to this substance and the extra amount formed by the action of double replacement has to fall out of the solution, that is, it is *precipitated.* In this way precipitates are formed on mixing solutions of two soluble substances which will yield an insoluble product. Such precipitates may be either crystalline or *amorphous* (lacking definite crystalline form).

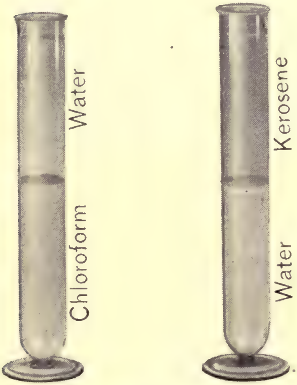


FIG. 19. — NON-MISCIBLE LIQUIDS.

73. Miscibility of Liquids. — "Oil and water will not mix" is an old way of saying that these two liquids do not dissolve in each other. If the oil is kerosene, it floats on top because it is lighter than water. Chloroform is insoluble in water, and, being heavier, sinks to the bottom. In both of these cases there is a very distinct boundary line between the two liquids (Fig. 19). When, however, grain alcohol is poured into water and the mixture shaken, neither liquid can be distinguished. We say that the two liquids are *miscible* (*i.e.* "mixable"). Each liquid is completely soluble in the other. Carbon disulphide and water are two non-miscible liquids. An *emulsion* is a case of non-miscibility where the particles of the two liquids remain intermingled. Cod-liver oil forms an emulsion with water. The fatty particles constituting the cream of milk are in a state of emulsion in fresh milk. Kerosene emulsion, used for killing plant lice, is made by agitating a mixture of soap, water, and kerosene.

Since two non-miscible liquids form two distinct layers, they may be easily separated by drawing off one of them. It is very difficult, however, to separate two miscible liquids, like alcohol and water, without resorting to some complicated process, such as fractional distillation.

74. Solution of Gases. — When a glass of water, freshly drawn from the tap, is allowed to stand at the room temperature, the sides of the glass often become coated with bubbles. These consist of gases which have been dissolved by the water. The water drawn from the faucet was colder than the temperature of the room. When the water was warmed to the room temperature, it could hold less of the dissolved gases. Unlike solids, *the solubility of a gas in a liquid is lessened with an increase of temperature.* The solubility of a gas in a liquid is usually expressed in terms of volume. The table on page 86 shows the relative solubility of some of the common gases and the effect of temperature on their solubility.

A few gases are exceedingly soluble in water. At the ordinary temperature 1 c.c. of water will dissolve 700 c.c. of ammonia, or nearly 450 c.c. of hydrogen chloride. Another way of stating the last fact is that 1 volume of

GAS	NUMBER OF C.C. DISSOLVED BY 100 C.C. OF WATER AT		
	0° C.	20° C.	100° C.
Hydrogen	2.15	1.82	1.60
Nitrogen	2.39	1.64	1.00
Oxygen	4.89	3.10	1.70
Methane	5.56	3.31	1.70
Carbon dioxide	171.30	87.80	
Chlorine	——	226.00	0.00
Ammonia	129890.00	71060.00	

water dissolves 450 volumes of hydrogen chloride. When vichy or seltzer is drawn from a siphon (Fig. 20) the water rushes out through the valve with a hissing noise. In the tumbler, streams of gas bubbles rise through the liquid and break at the surface. The gas which escapes so violently from the liquid is carbon dioxide, and its pressure is greater than that of the air into which it escapes. Evidently the pressure at which the carbon dioxide was dissolved in the water was much greater than the atmospheric pressure. In other words, increasing the pressure causes the water to dissolve a greater weight of carbon dioxide. Therefore it may be stated that *the weight of a gas dissolved increases with the pressure.* Bottled mineral waters or other highly effervescent beverages are charged with a soluble gas under pressure. Consequently the containers and stoppers must be strong. The pressure in a siphon soda bottle is 140 pounds

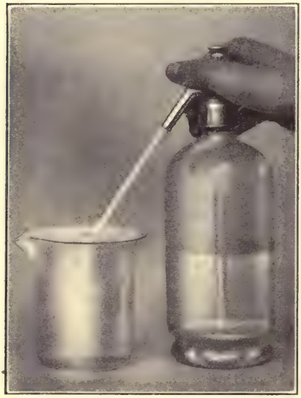


FIG. 20.

per square inch; in ginger ale bottles, 90 pounds; and in club soda bottles, 105 pounds. On the opening of the bottles, there is always danger that the sudden release of pressure at the stopper will allow the dissolved gas to rush out with such force as to burst a defective bottle. To avoid the danger of flying glass in such a case, it is always advisable to wrap a cloth around a bottle containing a charged liquid before opening it.

SUMMARY

A Solution is a mixture of uniform composition which does not follow the Law of Definite Proportions.

A Solvent is a substance which has the power of dissolving another substance.

A Solute is a substance dissolved.

Turbidity is due to small solid particles held in suspension. These in time will usually settle to the bottom.

Dilute and Concentrated are relative terms applied to solutions. The greater the amount of solute in comparison with the amount of solvent, the more concentrated is the solution. Concentrated solutions may be prepared by evaporating part of the solvent from the dilute solution.

A Saturated Solution of a substance is obtained when the solvent has dissolved all it can of that substance under the existing conditions, particularly as to temperature.

The Solubility of Most Solids in liquids increases with the temperature.

Precipitates are formed when the mixing of the solutions of two soluble substances yields an insoluble substance.

Crystallization is the separation of a dissolved solid in definite form and is usually due to the partial evaporation of the solvent, or to the cooling of the solution.

Miscible Liquids are those which are completely soluble in each other.

Gases decrease in solubility with an increase in temperature.

EXERCISES

1. What are the characteristics of a solution?

2. What is the greatest difference between the composition of a compound and of solutions of that compound?

3. Distinguish between solvent and solute.

4. Name five of the common liquid solvents.

5. What is the most widely used solvent?

6. How would you determine whether or not a solid is soluble in water?

7. State the difference between a dilute and a concentrated water solution of alum.

8. How would you prepare a saturated water solution of a very soluble substance? Of a moderately soluble substance?

9. How could you determine that the limewater sold in drug stores is simply a dilute solution?

10. Define a saturated solution.

11. How can you tell when a solution is saturated with respect to a particular substance?

12. What is the quickest way to make a cold saturated solution of boric acid?

13. What effect does the temperature have upon the solubility of most solids?

14. Compare the relative solubility of common salt and washing soda in hot and in cold water.

15. How would you obtain crystals of blue vitriol from some of the finely powdered substance?

16. Describe a case of precipitation by the action of double replacement.

17. What is meant when it is said that carbon disulphide and water are non-miscible?

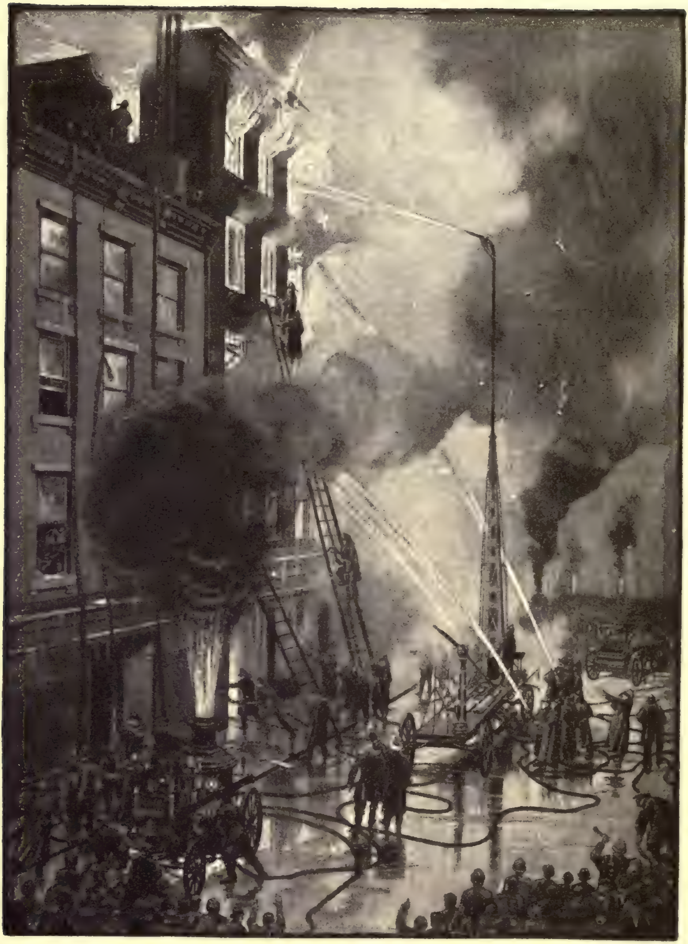
18. Name two miscible liquids. What is an emulsion?

19. Account for the bubbles seen in a glass of ginger ale.

20. Compare the solubility of oxygen in hot and in cold water. How does the solubility of oxygen in water differ from that of carbon dioxide?

21. What advantage is taken of the great solubility of ammonia for its transportation? What other gas is distributed in a similar manner?

22. Explain the dangers in handling bottles or siphons containing charged waters.



Courtesy of *The Century Co.*

FIG. 21. — FIGHTING FIRE.

CHAPTER X

BURNING AND OXIDATION

75. Burning. — When the strip of copper was thrust into the test tube containing boiling sulphur, the copper took fire and burned in the sulphur vapor (§ 8). A new substance, copper sulphide, was formed. In all ordinary cases of burning, however, chemical action takes place between the oxygen of the air and the substance burned. Oxides result from the chemical reaction, because the same substance is formed when a certain kind of matter is burned in air that is formed when that kind of matter is burned in oxygen. Remove oxygen from air and substances cease to burn. Sulphur burns readily in air, and the product of combustion has a characteristic odor. When sulphur is burned in pure oxygen, a gas, sulphur dioxide, is formed which has the same odor as the product obtained by burning sulphur in air. Steam, which may be readily condensed to water, is formed when hydrogen is burned in air, and also when hydrogen is burned in pure oxygen. Carbon dioxide, a colorless gas which causes limewater to become milky, is formed when carbon is burned in oxygen, and likewise when carbon is burned in air. If oxygen is removed from air, neither sulphur, hydrogen, nor carbon will burn in the remaining gases.

We commonly speak of the gas in which a substance burns as being a supporter of combustion, and of the substance burned as being combustible. These terms are simply convenient to use, for air will burn as readily in illuminating gas as illuminating gas will burn in air. I either case the burning is due to the fact that the illuminating gas and the oxygen of the air unite chemically wit rapidity.

76. Kindling Point. — All are familiar with the fact tha wood must be heated before it will take fire. There is fixed temperature below which it will not start to burn The lowest temperature at which a substance will burn i air is called its *kindling temperature*. The kindling poin of any one substance is constant. Materials, however vary greatly in their kindling temperature. This fact i made use of in an ingenious way in the construction of match. The ordinary parlor match (Fig. 22) consists of a small stick o wood, one end of whic has been soaked in paraffin and then dipped in a mixture of glue, phosphorus and some material which will readily give off oxygen. When the match is scratched, the friction cause sufficient heat to ignite the head of the match; this i burning raises the temperature of the paraffin to it kindling point, and the burning paraffin raises the temperature of the wood to its kindling temperature.

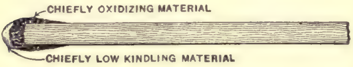
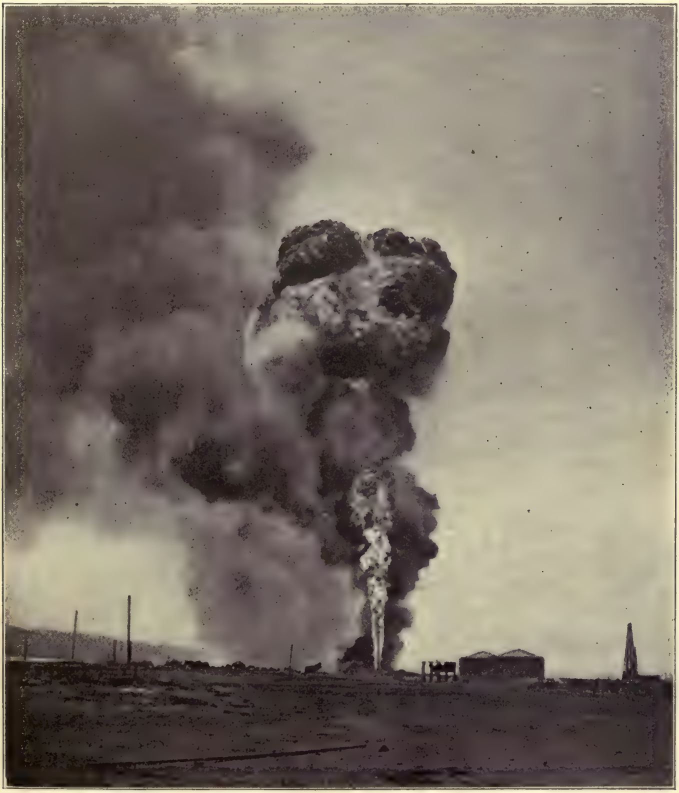


FIG. 22. — CROSS SECTION OF A MATCH.

77. A Fuel is a material that is burned for the purpos of obtaining heat. Both heat and light are produced whe a fuel burns, but sometimes heat and at other times ligh is the form of energy desired. All common fuels, such a wood, coal, kerosene, gasoline, and gas, contain carbon an hydrogen. The carbon may be largely uncombined, as i hard coal, or in chemical combination with hydrogen, a in the cases of kerosene, gasoline, and gas, or united wit hydrogen and oxygen, as in the case of wood. Compounds consisting of carbon and hydrogen only are called *hydrocarbons*. Acetylene and marsh gas are such compounds. Illuminating gas is a mixture of hydrogen, carbon monoxide, and various hydrocarbons.

78. Products of Combustion. — Two compounds of carbon and oxygen are known, carbon monoxide, CO, and carbon dioxide, CO_2. During the complete combustion of the



Courtesy of *The Scientific American.*

FIG. 23. — BURNING OIL WELL.

fuels mentioned, only two products result; namely, steam and carbon dioxide. As both of these compounds are colorless gases, they pass into the air unobserved. If smoke is formed during burning, it shows that the combustion is not complete, inasmuch as a part of the carbon has not been burned (Fig. 23). The ashes left in the stove when wood or coal is burned are due to the sand, clay, and various other kinds of mineral matter which were either contained in the fuel or mixed with it.

79. Conditions Necessary for Burning to Continue. — In order to have burning continue after being started, substances that will enter into chemical combination with each other (fuel and oxygen) must be supplied, the tem-

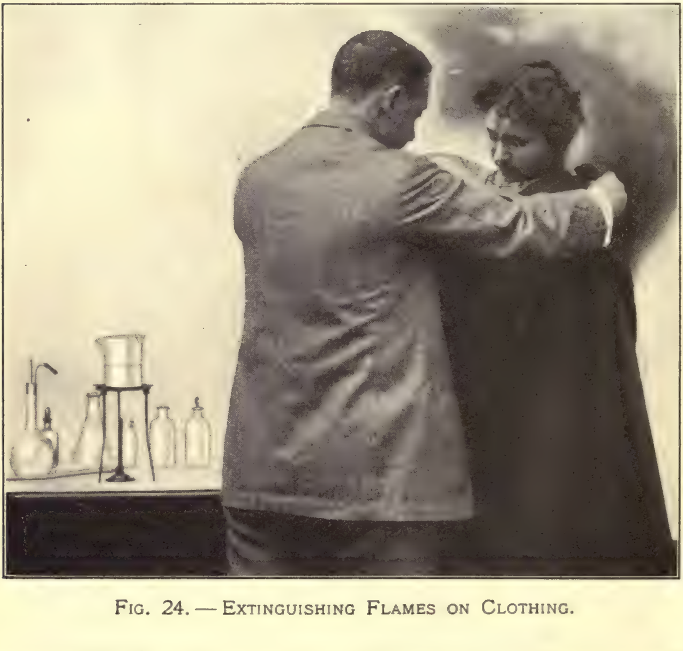


FIG. 24. — EXTINGUISHING FLAMES ON CLOTHING.

perature must be kept above the kindling point, and the products of combustion must be carried away. The removal of any one of these conditions will cause the fire to go out, and the methods employed for putting out fires depend upon this fact.

In the case of a burning building, water is the agency usually employed (Fig. 21). The water absorbs heat and lowers the temperature of the burning material below its kindling point. At the same time, the water and the steam produced from it lessen the amount of air in contact with the burning substance. In the case of a great conflagration, where the fire has spread over such an extended area that it is impossible to extinguish it by water, the combustible material is removed by dynamiting buildings. Other illustrations of the removal of the combustible substance are the back-firing of a forest, the plowing around a field of burning grass, and the carrying away of highly inflammable substances from the vicinity of the fire.

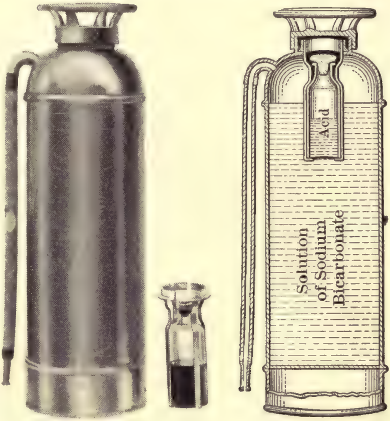


FIG. 25. — FIRE EXTINGUISHER.

The means most commonly employed to put out a small fire is to prevent the supporter of combustion from coming in contact with the burning material. A rug or similar article is thrown around a person whose clothing has caught fire (Fig. 24). Earth, or sand, is thrown on the burning substance. Fire extinguishers, which replace the air in contact with the burning material with a gas that does not support combustion, are used. The fire extinguisher shown in Fig. 25 is used to throw a stream of water charged with carbon dioxide on to the fire. When the extinguisher is inverted, the stopper falls out of the bottle, allowing the sulphuric acid to come in contact with the solution of sodium bicarbonate contained in the body of the extinguisher. Carbon dioxide is produced according to the equation:

$$\underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} + 2\,\underset{\substack{\text{sodium}\\ \text{bicarbonate}}}{NaHCO_3} \longrightarrow 2\,\underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2} + 2\,\underset{\text{water}}{H_2O} + \underset{\substack{\text{sodium}\\ \text{sulphate}}}{Na_2SO_4}$$

The pressure of the carbon dioxide generated forces the solution out through the hose. "Pyrene" extinguishers contain carbon tetrachloride, a highly volatile liquid, whose vapor does not burn.

80. Change of Energy during Burning. — Every chemical action is accompanied by a change of energy, heat being the form of energy most frequently taken into consideration. In some instances, heat is absorbed during a chemical change, so that the compound formed contains more energy than its constituents did. When acetylene is formed from the elements carbon and hydrogen, a large amount of energy is absorbed; consequently, when acetylene is burned, more heat is liberated than would be produced by burning equivalent weights of uncombined carbon and hydrogen. More frequently, however, heat is liberated during a chemical change. When this is of sufficient intensity to produce light, burning is said to take place. *Burning* is chemical action accompanied by light and heat.

81. Slow Oxidation. — Everybody is familiar with the fact that iron rusts when exposed to air. Thin layers of linseed oil left in contact with air are converted into a leathery substance, the "skin" which forms on the surface of a linseed oil paint when left standing in an open can. Carbon in the tissues of the body is converted into carbon dioxide. In all of these cases, oxidation has taken place, but the process has gone on so slowly that no light has been produced, and the temperature has remained low. These examples illustrate the process of *slow oxidation.*

In certain cases, we do not want oxidation to take place; for example, we do not want iron to rust, so we prevent the oxygen of the air from coming in contact with the iron by covering it with some substance such as paint, stove polish, zinc, tin, or nickel. In other cases oxidation is desirable. Paints contain some oil which will oxidize to produce a leathery substance capable of holding the color to the surface of the material painted. Oils which absorb oxygen and are converted by the process into solids, are called *drying oils.* Linseed oil, fish oil, and China wood oil are the principal ones used in paints. Since linseed oil absorbs oxygen so slowly that during the drying there would be time for particles of dust to settle on the wet paint, some substance, called a *drier*, is added to the paint to hasten the process.

If the heat formed during slow oxidation is not carried away by the air as rapidly as it is produced, the body being oxidized will grow warmer and its kindling temperature may finally be reached. Spontaneous combustion is generally brought about in this way.

During the formation of carbon dioxide in the body, the oxygen taken up by the blood in the lungs slowly unites with the carbon compounds in the body. The heat of the body is due to this reaction. If the oxidation takes place too rapidly, fever results; if too slowly, a temperature below normal is produced. In the latter case, doctors often administer oxygen to increase the rapidity of the oxidation.

The same amount of heat is generated whenever a gram of carbon is converted into carbon dioxide. If the time consumed in the oxidation is long, the temperature may remain low and no light will result. The process is then called *slow oxidation.* If the time consumed is short, the kindling temperature will be reached and the process will then be one of *combustion.*

SUMMARY

Burning is chemical action accompanied by noticeable light and heat. When a substance burns in air the same compound is formed as when that substance is burned in oxygen. This may be readily illustrated by burning an element whose product of combustion can be easily recognized. When oxygen is removed from the air, burning stops.

The gas in which a substance burns is commonly called the **Supporter of Combustion**, and the substance burned is said to be the **Combustible**.

The Kindling Point of a substance is the lowest temperature at which that substance will burn in air. The kindling temperature varies greatly with the kind of matter.

A Fuel is combustible matter used to produce heat. Carbon and hydrogen are the principal elements of value in all common fuels, and carbon dioxide and steam are the products of the combustion desired. Ashes and smoke are undesirable.

Conditions Necessary for Burning are a temperature at least as high as the kindling point of the combustible substance and a supply of fuel in contact with the supporter of combustion. A removal of either of these conditions will cause the fire to go out.

A compound may contain more energy than do the elements of which it is composed when they are in a free condition.

Slow Oxidation is the chemical combination of a substance with oxygen at so slow a rate that noticeable light is not produced.

When the heat produced by slow oxidation accumulates, **Spontaneous Combustion** frequently occurs. Familiar illustrations of slow oxidation are the rusting of iron, the hardening of surface layers of linseed oil on exposure to air, and the production of carbon dioxide in the body.

EXERCISES

1. Define burning.

2. Does burning ever take place in the absence of oxygen? Give evidence to prove your answer.

3. Mention cases to illustrate the fact that during ordinary burning, oxides are formed.

4. Why is oxygen called a supporter of combustion, while nitrogen is said not to support combustion?

5. Is oxygen the only element that will support combustion? Explain.

6. Define kindling point, kindling temperature, or ignition point.

7. Show how the structure of a match illustrates the fact that all substances have not the same kindling point.

8. Is paper used in starting a fire because it has a lower kindling temperature than wood? Give reasons for believing your answer to be correct.

9. From a chemical standpoint, what is smoke?

10. Why is it more difficult to burn soft coal than hard coal without producing smoke?

11. Give a practical illustration of putting out a fire by (*a*) lowering the temperature of the burning material below its kindling point; (*b*) the removal of the combustible substance; (*c*) preventing the supporter of combustion from coming in contact with the combustible material.

12. Name a compound of carbon and hydrogen which when burned yields more heat than could be obtained by burning the same weight of carbon and hydrogen in a free condition.

13. Define slow oxidation. Why should not the term *combustion* be used in connection with slow oxidation?

14. Why is iron often coated with tin, zinc, or nickel?

15. Why are substances often added to paint to increase the rapidity with which the linseed oil takes oxygen from the air?

16. State the conditions necessary for spontaneous combustion.

17. Why does a person require more food in winter than in summer?

18. Why is pure oxygen often administered to a person having pneumonia, a disease by which the effective lung area is decreased?

19. What happens when oxidation takes place in the body with more than normal rapidity?

20. How would the amount of heat obtained by burning a gram of carbon in oxygen compare with that liberated when a gram of carbon is converted into carbon dioxide in the body? How would the temperatures in the two cases compare? Explain.

CHAPTER XI

FUELS

82. Definition of Fuels. — Fuels are substances that unite readily with the oxygen of the air, giving off a considerable amount of heat in the process, and are cheap enough to be used in large quantities for practical purposes. The characteristics desirable in them are:

(*a*) high calorific power; that is, the property of furnishing a large amount of heat per unit of weight;

(*b*) low per cent of ash;

(*c*) freedom from objectionable products of combustion;

(*d*) low cost of production;

(*e*) ease of transportation and handling.

SOLID FUELS

83. Wood has been used as a fuel from earliest times. It has most of the desirable characteristics, but since it is no longer a cheap article in many localities, it is not so much used as formerly. Wood consists chiefly of the chemical compound cellulose, $(C_6H_{10}O_5)_n$. When it burns, carbon dioxide and water are formed.

$$\underset{\text{cellulose}}{C_6H_{10}O_5} + \underset{\text{oxygen}}{6\,O_2} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{6\,CO_2} + \underset{\text{water}}{5\,H_2O}$$

The ash that is left when wood or other fuel burns is a residue of incombustible mineral matter. Water is always present in wood. In freshly cut wood there may be as high as 50 %, and even after thorough drying by long standing, as much as 20 % may remain. The presence of water in any fuel lessens the heat value. The best woods for heating purposes are the hard varieties, such as maple and oak, which do not burn rapidly.

84. Flames. — The flame that is seen during the combustion of most fuels consists of burning gases, which have been driven out by the heat of the combustion. Particles of carbon are frequently liberated by the decomposition of these gases during the process of burning, and, being heated white hot, they make the flame luminous. The presence of carbon particles is readily proved by the fact that a cold object placed in contact with the flame becomes covered with soot. A flame that does not carry particles of free carbon, as, for example, the flame of burning hydrogen, or that of a Bunsen burner, is not luminous.

85. Coal. — This is by far the most important of all fuels. Most of the commercial enterprises of the world depend on its use. We mine this indispensable article from deposits which were stored up millions of years ago at a time when peculiar conditions existed on the earth's surface. A dense vegetation flourished in swamplike land. On falling, it became buried under mud and water, so that oxygen did not have access to it. Thus decay in the usual manner could not occur. If it had, the carbon would have been returned to the air in the form of carbon dioxide, but, under the conditions that existed, the carbon remained and was transformed into coal. According to the extent of the transformation, we find different varieties. The two chief kinds are bituminous or soft coal, and anthracite or hard coal.

86. Bituminous Coal. — This variety of coal has undergone less decomposition than anthracite. The cellulose of which it was originally composed has been so changed that from 50% to 75% of the weight is *uncombined carbon.* From 15% to 40% of the remainder is composed

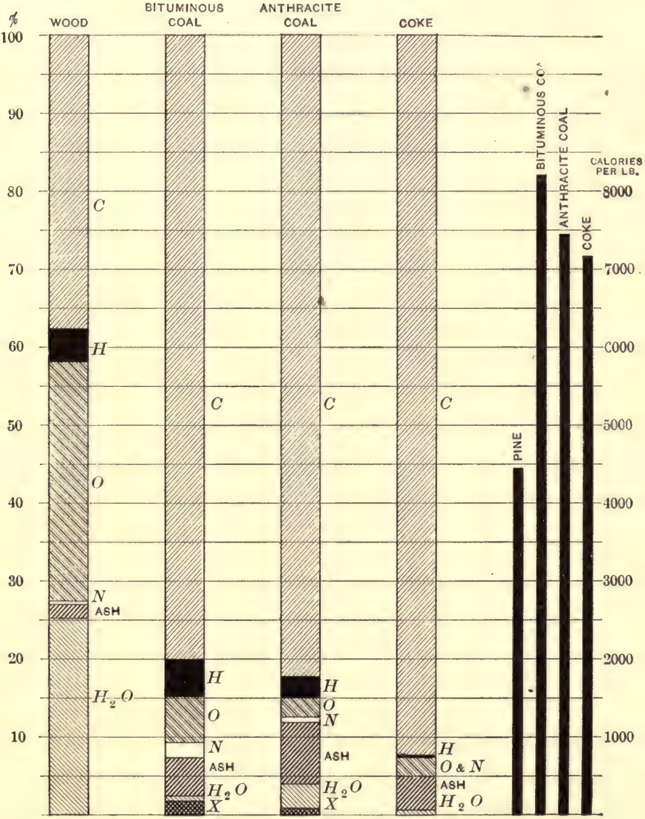


FIG. 26. — COMPOSITION AND HEAT VALUE OF COMMON FUELS.

of compounds known as *hydrocarbons.* These are distilled from the coal as it burns, and give a smoky, luminous flame. The "softer" the coal, the more smoky the flame. For most purposes this is an undesirable characteristic. Cities in which soft coal is used are notorious as "dirty" cities. Furnaces in which such fuel is used should be arranged to consume the sooty matter.

Soft coal has many advantages. It has high heat value, is easily kindled, and burns very quickly. It is the chief fuel used in industrial operations.

87. Anthracite Coal. — This variety is found only in mountain regions where nature subjected the buried vegetable matter to much heat and pressure during the changes that took place in the process of mountain formation. As a result the coal lost much of its volatile matter. It contains from 80% to 90% of uncombined carbon, and from 5% to 10% hydrocarbons. Consequently it burns with almost no flame. This makes it a very clean fuel, admirably adapted for use in cities.

88. Ash from Coal. — Both varieties of coal leave a considerable amount of ash on burning. The per cent of ash varies greatly in different varieties of coal, and in different grades of the same variety. It is the most important factor in determining the comparative heating value of different samples of coal. The true ash is the residue of mineral matter which was absorbed from the earth by the growing plant. In addition, there is apt to be present in coal a certain amount of slate, which is merely the hardened clay that became imbedded in the coal during the process of its formation. In good grades of coal most of the slate is removed when it is prepared for the market. In lower grades, much of the slate remains, and in such cases there may be as high as 30% to 35% of ash after the coal is burned.

89. Fuels related to Coal. — There are several of these fuels not much used in this country. The important ones are:

Peat, formed from moss that has been buried under water; it contains much ash and a high per cent of water.

Lignite, a form of coal in which the vegetable matter has been so little changed that it still resembles wood.

Cannel Coal, a form of soft coal very rich in hydrocarbons. It burns with much flame, making a beautiful fire for open grates.

Briquettes, a manufactured fuel much used in Europe, and rapidly coming into use in this country. The powdered coal that is formed in mining and preparing the article for the market, and which would otherwise be a waste product, is mixed with tarry matter and compressed into molds.

LIQUID FUELS

90. Petroleum. — This is the most important of liquid fuels. Like coal, it is a deposit that was formed ages ago within the earth. Little is known of its origin. Within recent years petroleum has come into use in its unrefined state as an important fuel for railroads, steamships, and factories. It competes successfully with coal in those parts of the country where it occurs and where coal is scarce. This is particularly true in Texas and California. It has a high heat value, and the important property of leaving no ash. In addition, since it is a liquid, it can be transported in pipe lines, often for hundreds of miles. This is a very important economic consideration.

91. Refining of Petroleum. — Petroleum as it is found within the earth consists of a mixture of many hydrocarbons. By a process of distillation these are very easily separated, and various products are obtained. The crude oil is heated, and gases that pass off are again turned into liquids by condensation. The distillation is partly of the *destructive* variety; that is, a certain amount of chemical decomposition is effected in the original petroleum. By this means the nature of the products can be varied to meet commercial needs. The products range from light, low-boiling oils, like gasoline, to the heavy oils that are used for lubricating machinery.

FIG. 27. — OIL FIELD.

The process of petroleum refining also includes treatment to remove impurities, such as sulphur compounds, which would form undesirable products of combustion. This subject is more fully treated in Chapter XXXII.

92. Gasoline. — This article, considered an undesirable product in the early history of petroleum refining, has of recent years become one of the most valuable, owing to the increasing use of gasoline engines in automobiles, motor boats, and for many other purposes. Gasoline is formed by the condensation of gases that pass off at comparatively low temperatures during the distillation of petroleum. Its valuable characteristic is its volatility; that is, the ease with which it becomes a gas. This same characteristic is also the cause of many accidents in handling gasoline. *Its vapor, when mixed with air, is highly explosive.* It is dangerous only under these conditions.

Gasoline is a mixture of hydrocarbons whose chemical composition can be represented by the general formula $C_n H_{2n+2}$, in which n stands for the number of carbon atoms. Using one of these hydrocarbons, hexane, C_6H_{14}, as a type, the equation for the burning of this kind of fuel is

$$\underset{\text{hexane}}{2\,C_6H_{14}} + \underset{\text{oxygen}}{19\,O_2} \longrightarrow \underset{\substack{\text{carbon}\\\text{dioxide}}}{12\,CO_2} + \underset{\text{water}}{14\,H_2O}$$

93. Kerosene. — The character of this fuel is best understood by comparing it with gasoline, which it in general resembles, except that it is much less volatile. It is obtained from the crude petroleum at a temperature just above that at which gasoline passes off. Its chief use is as an illuminant in lamps. It is also increasingly used as a fuel in cooking stoves, where a city gas system is not available, and for the operation of the kerosene engine.

94. Alcohol. — Although at present used as a fuel on only a very small scale, alcohol is nevertheless of importance in this connection. Its heat value is very high, and it burns with a clean flame. The chemical composition is represented by the formula C_2H_5OH; the equation for the burning is

$$\underset{\text{alcohol}}{C_2H_5OH} + \underset{\text{oxygen}}{3\,O_2} \longrightarrow \underset{\substack{\text{carbon}\\\text{dioxide}}}{2\,CO_2} + \underset{\text{water}}{3\,H_2O}$$

Alcohol is adapted for use in cooking or heating on a small scale, especially where transportation is a difficult matter, as in Arctic exploration or mountain climbing. It has been used successfully as a fuel for gas engines, and it may ultimately be the chief fuel for this purpose, since the supply of petroleum within the earth is limited. Alcohol is made by the fermentation of vegetable matter and can be produced indefinitely in any quantity.

GASEOUS FUELS

95. Coal Gas. — The gas obtained by heating soft coal until it decomposes chemically, came originally into use solely as an illuminant. But, as the process of manufacture improved, and as uses were found for the by-products, the cost of producing the gas was so reduced that it has now come into use as a fuel. In large cities it is the most important fuel for cooking purposes. It has numerous points of superiority for this use. It can be distributed through pipes at low cost, it burns with a clean flame, the heat can be concentrated in one spot, and no handling of fuel or ashes is necessary.

The process of destructive distillation by which coal gas is obtained consists in heating bituminous coal in retorts without access of air. A variety of products is obtained, including the by-products named below. The gas is collected in gas tanks after undergoing a certain amount of purification. It consists of a mixture of gases in approximately the per cents named.

	%
Hydrogen	47
Methane, CH_4	40.5
Carbon monoxide, CO	6
Ethane, C_2H_6	4
Carbon dioxide, nitrogen, oxygen, total of	2.5

Other hydrocarbons of high illuminating power occur in small amounts.

An important by-product of the coal gas process is *coke*, which is itself a very important fuel. It has a chemical composition similar to that of hard coal, but it burns more rapidly, because it is porous in structure. It can be used as a substitute for hard coal. It is used on a large scale in producing iron from iron ore (Chapter XL).

Coal tar and *ammonia* are two other important by-products of coal gas manufacture. Their extraction and uses are described in Chapter XXXII.

96. Water Gas. — This fuel and illuminant is, like coal gas, a manufactured product. The operation makes use of the fact that steam reacts with incandescent carbon and forms hydrogen and carbon monoxide:

$$\underset{\text{carbon}}{C} + \underset{\text{steam}}{H_2O} \longrightarrow \underset{\text{carbon monoxide}}{CO} + \underset{\text{hydrogen}}{H_2}$$

Either hard coal or coke may be used as a source of the carbon. It is brought to a state of incandescence by blowing a blast of air through it for a few minutes. The white-hot fuel is then exposed to the action of steam, and the reaction described above takes place. The coke is not allowed to cool below 1000°. When this temperature is reached, air is again blown in. These alternations occur about every fifteen or twenty minutes. Both of the gaseous products are combustible, and hence the process obviously produces a cheap fuel. When the gas is to be used as an illuminant, a further step is essential, since the mixture of carbon monoxide and hydrogen burns with a non-luminous flame. To render the flame luminous, an admixture of hydrocarbons is necessary. This operation is called "enriching" the gas. It consists in spraying in gas oil, and subjecting the mixture to a high temperature, so that the liquid hydrocarbons are converted permanently into gases. When the water gas burns, these are decomposed by the heat of the flame, and particles of carbon exist for a brief instant in the free state, and become heated to the point at which they emit light.

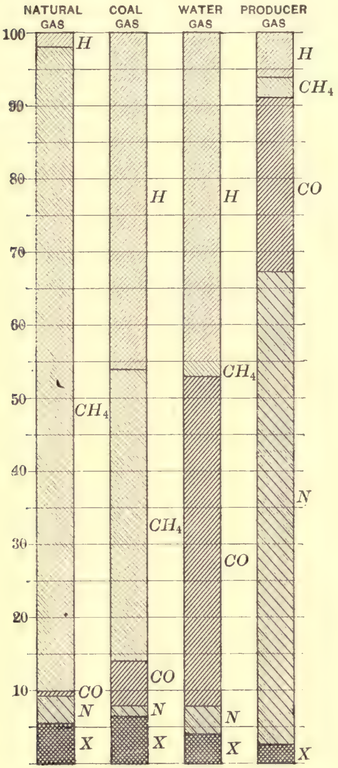


FIG. 28. — VOLUME COMPOSITION OF FUEL GASES.

X = Minor Constituents.

Water gas has less heat value than coal gas and is more dangerous in case of leakage, because it has a higher per cent of carbon monoxide, which is a very poisonous substance.

97. Producer Gas. — Producer gas is used as a fuel only, chiefly for gas engines (Chapter XXXIV) and in metallurgical and other manufacturing operations. It is made at a low cost by blowing air through incandescent coke or coal. It consists of carbon monoxide mixed with much nitrogen. Sometimes steam is blown in with the air blast, in which case the product contains some hydrogen. The heat value of producer gas is low, but this is offset by the low cost of production.

98. Natural Gas. — A gas of low illuminating power and high heat value is found stored in some parts of the earth. It is contained in a highly compressed state in the pores of rocks. By drilling wells to these strata it can be made available as a fuel. In many parts of the country it is the chief fuel. It is composed mainly of the hydrocarbon methane, CH_4. Natural gas is always found associated with petroleum deposits.

99. Acetylene. — This gas is used chiefly as an illuminant, and its use for this purpose is discussed in Chapter XIV. It has an important use as a fuel in connection with the oxyacetylene burner, a means of obtaining an extremely high temperature. The burner is so arranged that the acetylene is mixed with oxygen at the moment it issues from the jet. The result is a small flame of intense heat, so hot that it will, for example, melt steel quickly. This gives a very quick and convenient means of cutting steel beams and plates (Chapter XXXIII).

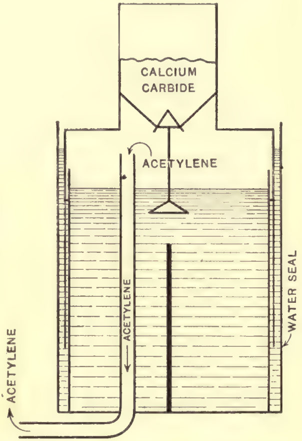


Fig. 29.—Acetylene Generator.

Calcium carbide is necessary in the production of acetylene for commercial purposes. This substance is made by heating coke with quicklime in the electric furnace, which develops a temperature sufficiently high for the following reaction to occur:

$$\underset{\text{carbon}}{3\,C} \quad + \quad \underset{\text{quicklime}}{CaO} \quad \longrightarrow \quad \underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} \quad + \quad \underset{\substack{\text{carbon}\\\text{monoxide}}}{CO}$$

When calcium carbide comes in contact with water, acetylene is rapidly formed:

$$\underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{acetylene}}{C_2H_2} + \underset{\substack{\text{slaked}\\\text{lime}}}{Ca(OH)_2}$$

SUMMARY

Fuels are Desirable in proportion as they have the following properties in a high degree: (*a*) high heat value, (*b*) low per cent of ash, (*c*) freedom from undesirable combustion products, (*d*) low cost of production, (*e*) ease of transportation and handling.

Important Solid Fuels are coal, wood, and coke. They contain carbon or carbon compounds as the combustible. Different varieties of coal contain from 50% to 90% of free carbon, the remainder being hydrocarbons and ash. Bituminous coals have a high per cent of hydrocarbons, varying from 15% to 40%. Wood consists mostly of cellulose, $(C_6H_{10}O_5)_n$.

Important Liquid Fuels are kerosene, gasoline, crude petroleum, and alcohol. The first three are mixtures of hydrocarbons; alcohol is the hydroxide of a hydrocarbon. Liquid fuels have the great advantage of leaving no ash, and of being very easy to transport and handle.

Important Gaseous Fuels are coal gas, water gas, producer gas, and natural gas. They consist of hydrogen, hydrocarbons, and carbon monoxide, or mixtures of these. Their convenience is so great that they are increasingly used, and they could be employed for most fuel purposes if their cost were not comparatively high.

Flames are burning gases. Luminosity in flames is caused by the presence of particles of free carbon that are heated to incandescence. Flames in which free carbon is not produced during the act of combustion are non-luminous.

Ash is the residue of incombustible mineral matter originally present in the vegetable matter from which the fuel was derived.

EXERCISES

1. Under similar conditions of air supply, which fuel would burn most slowly: wood, soft coal, or hard coal? Why?

2. Why does wood snap and crackle when it burns?

3. Why does maple make a better stove wood than white pine?

4. Which kind of coal burns with much flame? Why?

5. Why is the flame from cannel coal exceedingly luminous?

6. Why is it more desirable to burn waste coal dust in the form of briquettes instead of as the original powder?

7. How could you determine the per cent of hydrocarbons in a sample of coal? The per cent of ash?

8. In coal mines impressions of fern leaves, tree trunks, etc., are sometimes found. How do you account for this?

9. What defect exists if densely black, sooty smoke issues from a factory chimney? How could the trouble be remedied?

10. Why would it be dangerous to use gasoline in lamps?

11. Which fuel, kerosene or gasoline, is most used in gas engines? Why?

12. Why do we not use crude petroleum in lamps?

13. What are the chief differences in the composition of coal gas and water gas? Of producer gas and water gas?

14. What reasons can you assign for the growing popularity of gaseous fuels for cooking purposes?

15. Acetylene gives an exceedingly luminous flame. Explain.

16. Why do coals differ in their per cent of ash?

17. Define a fuel; a flame.

18. Name compounds that are formed in the combustion of wood; of coal; of kerosene; of illuminating gas.

19. Compare kerosene and alcohol as fuels.

20. When alcohol is burned what becomes of the oxygen that it contains?

CHAPTER XII

FIREPLACES AND STOVES

100. The Fireplace is a primitive arrangement for the indoor use of fire. A fireplace (Fig. 30) is a cavity walled with fireproof material, usually either brick or stone, built into one side of the room, and opening into a chimney. Wood is the form of fuel generally used. In order to increase the surface of the fuel in contact with the air, the wood is placed upon andirons, which hold it above the coals and ashes. An apron, or blower, which is a sheet of metal supported on legs, may be put in front of the fire. When the blower is placed properly, there is a strong draft under and upward between the sticks of wood, so that the gaseous products of combustion, together with the unconsumed portions of the air, are carried rapidly out of the chimney. Under these conditions, the fire, once started, burns brightly, but nearly all of the heat passes up the chimney. When the blower is removed, less air passes between the sticks of wood and the draft is diminished so that the fuel burns less rapidly, while more of the heat enters the room. The draft may be still further decreased by partly closing the chimney by a damper.

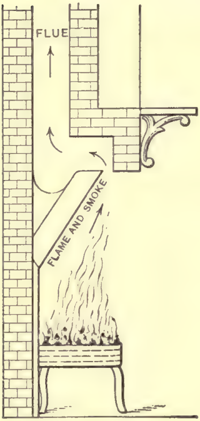


Fig. 30. — Section of a Fireplace.

There is no device for obtaining artificial heat that is so cheerful as the open fireplace, and there is none that is more wasteful. From 80 % to 90 % of the heat from the burning fuel is usually permitted to pass up the chimney without increasing the warmth of the room. Recently devices have been invented for using the hot gases as they pass up the chimney to warm a secondary current of air which enters the room. In this way the efficiency of the fireplace has been greatly increased.

If it were not for the pleasure to be derived from sitting by an open fire, watching the glowing coals and the fantastic shapes taken by the flames, the open fireplace would long since have passed out of use in most localities. The gas log and asbestos grate are poor substitutes for the open fireplace. When gas is used as fuel, the products of combustion are frequently allowed to mingle with the air of the room. While this lessens the waste of heat, it greatly diminishes the purity of the air.

101. Stoves. — A stove is a nearly closed receptacle, generally made of iron, in which fuel is burned for obtaining heat. When coal or wood is used as fuel, a system of drafts and dampers regulates the supply of air that enters the stove. The principles involved may be illustrated by a description of the ordinary coal stove used for heating purposes. In the front of the stove, at a lower level than the grate on which the coal is placed, is a row of openings, the *draft*, with a slide for closing them. A similar row of openings, also provided with a slide, placed at a higher level than the fuel, constitutes the *check*. In the stovepipe is a sheet of iron, the *damper*, arranged so that it either slides or may be turned to any degree between a vertical and a horizontal position.

To start a fire in the stove, crumpled pieces of paper or shavings are placed on the grate and small pieces of wood are laid loosely upon them. The check is closed and the draft and damper are opened. The pieces of paper, or the shavings, are then lighted. Only a small quantity of heat is required to raise the temperature of the edge of a piece of paper to its kindling point, and the burning paper soon sets the wood on fire. Air is drawn through the draft and passes between the pieces of wood, causing them to burn rapidly. At the same time, the products of combustion in gaseous form are carried away through the chimney. As soon as the wood is burning briskly, a small amount of coal is placed on the fire. When this first portion of coal has become thoroughly ignited, more coal is added to fill the fire box. Coal should never be placed above the lining of the fire box as the lids of the stove are damaged by overheating.

The temperature of the stove is regulated by manipulating the draft, damper, and check. When the draft is closed, only a small quantity of air enters the stove. This quantity may be still further diminished by closing the damper in the pipe. If the check is opened, the draft closed, and the damper nearly shut, cool air passes over instead of between the pieces of coal. Under these conditions only a small portion of the air which enters the stove is heated to the kindling point of the coal, and combustion takes place very slowly.

When the draft and damper are both open, the oxygen of the air, entering the bottom of the fire box and coming in contact with the lower layer of hot coal, first unites with the carbon to form carbon dioxide :

$$\underset{\text{carbon}}{C} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

If the carbon dioxide thus formed does not pass too rapidly through the upper layers of hot coal, it combines with more carbon so that carbon monoxide is formed:

$$\underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2} + \underset{\text{carbon}}{C} \longrightarrow \underset{\substack{\text{carbon}\\ \text{monoxide}}}{2\,CO}$$

Carbon monoxide is a very poisonous gas and should never be allowed to escape into the room. The blue flame frequently seen on top of the coal is burning carbon monoxide. When the check is open, the carbon monoxide is likely to be burned to carbon dioxide:

$$\underset{\substack{\text{carbon}\\ \text{monoxide}}}{2\,CO} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{2\,CO_2}$$

The damper should never be closed so tightly that the gaseous products of combustion will not escape into the chimney. A sleeping room should never contain a coal fire in a stove with the damper entirely closed, because carbon monoxide is likely to be formed and to escape into the room while the occupants are asleep. Many persons have lost their lives by breathing air poisoned by carbon monoxide from a stove near their beds. Although pure carbon monoxide is odorless, other gases having odors are formed during the burning of coal so that, if a person is awake, the escape of gas into the room will be noticed. Ashes should not be allowed to accumulate in a coal stove, as they prevent air from entering the draft. They should be shaken into the pan below the grate and removed daily.

102. Wood Stoves. — A wood stove differs from a coal stove chiefly in the form of the grate; in fact, wood stoves frequently have no grate, the draft being placed just above the space intended for ashes.

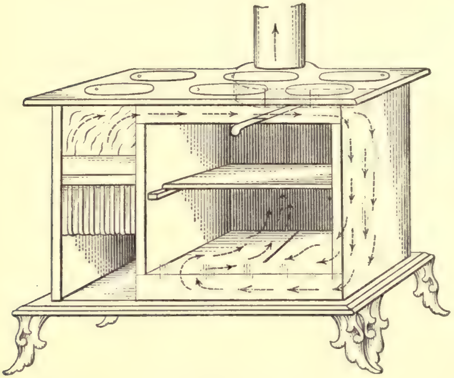


FIG. 31. — KITCHEN RANGE — SMOKE DAMPER CLOSED.

103. The Kitchen Range. — Cook stoves, in addition to the draft, damper, and check, have a *smoke damper*. When the smoke damper is closed (Fig. 31), the hot, gaseous products of combustion pass around the oven before entering the chimney, and the oven becomes heated. If the smoke damper is open (Fig. 32), there is direct communication, over the oven, between the fire box and chimney, so that only the top of the oven is warmed. Dust, carried with the gaseous products of combustion, is deposited on top and under the oven. This deposit is a poor conductor of heat and obstructs the passage of the gases under the oven. It must be removed occasionally or the oven will not be heated as it should. Often the top of the oven is so constructed that all of the ashes cannot be easily removed.

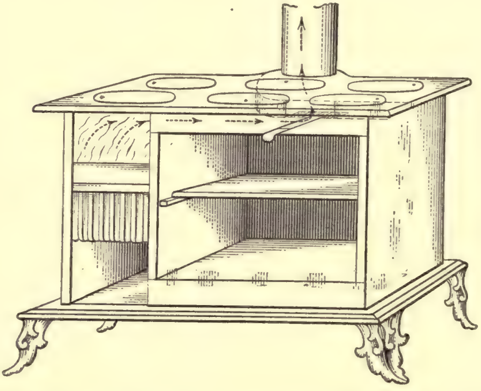


FIG. 32. — KITCHEN RANGE — SMOKE DAMPER OPEN.

104. Furnaces. — A furnace is an arrangement for heating a house indirectly. Three classes of furnaces are in common use: the hot-air furnace (Fig. 33), the hot-water furnace, and the steam furnace. Considering these in the order named, the combustion of the fuel is used to heat air, to warm water, or to convert water into steam. The heated air is conveyed through large pipes to the various rooms to be warmed. The steam or hot water passes through pipes to radiators set in the rooms to be heated. In the radiators, the steam or hot water is cooled, and then returns through pipes to the furnace, the heat meanwhile entering the rooms. One fire thus provides heat for the whole house, and the fuel and ashes are kept out of the living rooms.

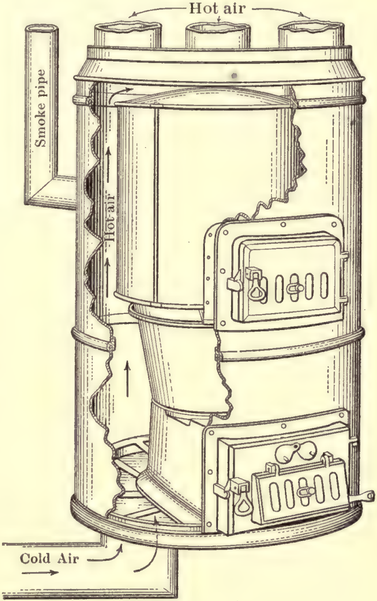


Fig. 33. — Hot-air Furnace.

SUMMARY

An Open Fireplace is a walled space built into one side of a room, in which fuel may be burned. Andirons are used to keep the fuel above the ashes, and an apron or blower is used to increase the draft between the pieces of fuel. The open fireplace is the most cheerful arrangement for warming a room, but is most inefficient.

Gas Logs and **Asbestos Grates** are substitutes for open fireplaces. The products of combustion are often permitted to mix with the air of the room, which is thus made impure.

A Stove is a nearly closed receptacle in which fuel is burned. A heating stove is generally provided with a draft, a check, and a damper. The **Draft** permits air to enter the stove beneath the grate. The **Check** permits air to enter above the grate. The **Damper** regulates the size of the opening through which products of combustion escape to the chimney.

The Kitchen Range has, in addition to the draft, the check, and the damper, a Smoke Damper which can be used at will to guide the products of combustion directly into the chimney, or cause them first to pass around the oven. The space under the oven should be kept nearly free from ashes, but a thin layer of ashes should be allowed to accumulate on top of the oven to prevent overheating.

The Furnace is a form of stove, generally placed in the cellar, used to heat air or water, by means of which the heat of the burning fuel is indirectly carried to the living rooms. Modern furnaces are economical and tend to keep the living rooms clean.

Paper or shavings are used **to start a fire** because a very small quantity of heat is required to bring the temperature of this thin material to its kindling point, and because they present a large surface to the air. Burning wood is used to raise the temperature of the coal to its kindling point.

The principal **products of combustion** when hard coal is used as fuel are carbon dioxide and carbon monoxide. Carbon monoxide should be burned to carbon dioxide. Carbon monoxide is a deadly poison and should never be permitted to enter a living room.

EXERCISES

1. What is the chief advantage of an open fireplace? The principal disadvantage?

2. Make a drawing of a coal stove used for heating. Show the location of the grate, the draft, the check, and the damper.

3. Should (1) the damper, (2) the check, and (3) the draft be opened or closed (*a*) when the fire is started? (*b*) In order to have the fire keep as long as possible?

4. Does opening the check cause the fire to burn more or less rapidly? Explain.

5. Why is the use of the check a wasteful method of regulating the rapidity of burning?

6. Give directions for starting a coal fire.

7. Why may either paper or shavings be used in starting a fire?

8. What two oxides of carbon are formed during the burning of coal in a stove?

9. Why should not carbon monoxide be permitted to mix with the air of a living room?

10. How does a kitchen range differ from a heating stove?

11. Tell how the (*a*) check, (*b*) draft, (*c*) smoke damper, and (*d*) damper should be manipulated for a "quick oven." For a "slow oven."

12. What most frequently causes a stove to bake poorly after it has been in use for some time?

13. How can an oven be prevented from baking "too hard on top"?

14. What is the chief disadvantage in using a stove to heat a room?

15. What are some of the advantages in the use of a hot-water system for heating? A disadvantage? *

16. What is the chief advantage of a steam-heating plant? The principal disadvantage? *

17. What great advantage has a hot-air system over a hot-water or a steam-heating system? *

* Exercises 15, 16, and 17 are for class discussion.

CHAPTER XIII

GAS AND GASOLINE STOVES

105. The Bunsen Burner. — Before considering the gas range it may be well to make a study of the burner universally used in chemical laboratories as a source of heat. Its chief advantage is that it gives a hot, smokeless flame. This burner bears the name of the distinguished German chemist who invented it, Robert Wilhelm Bunsen. The bunsen burner (Fig. 34) consists of three parts: the base, the barrel, and the ring. The base is provided with a horizontal tube (for attaching a rubber hose to connect the burner with a gas cock) and a small, central gas way or "spud," through which the gas passes to the barrel. The barrel is a metal tube, with two or more holes near the lower end, made to screw on the base. The ring fits the lower end of the barrel, and has holes which may be either brought over those in the barrel, or over its solid portion.

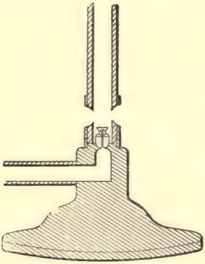


FIG. 34. — SECTION OF BUNSEN BURNER.

When the burner is in use, gas enters the barrel through the spud, mixes with a supply of air only partially sufficient for complete combustion, and the mixture rises to the top of the barrel, where it is ignited and burns in the surrounding air. The air entering the holes at the base of the barrel is termed "primary air," and is secured by the gas issuing at a high speed from the spud. This stream of gas produces a partial vacuum in the barrel, causing air to enter the holes near its base, and to mix with the gas before leaving the burner. The supply of gas and air should be adjusted so that a non-luminous flame of suitable size is obtained, and so that the flame will not "strike back." The supply of gas entering the barrel is regulated by varying the size of the opening in the spud, and the supply of air which mixes with the gas is regulated by turning the ring so as to vary the size of the holes through which the air enters the barrel. If the gas pressure is low, the mixture of gas and air may burn downward more rapidly than it issues from the barrel. In this case, the burner will *strike back;* that is, the flame will pass down the barrel to the end of the spud, at which point incomplete combustion will take place. This not only produces a disagreeable odor, but is likely to heat the base of the burner sufficiently hot to melt the rubber hose, and the escaping gas may be set on fire.

In the inner portion of the bunsen flame, the gas is only partly burned, and, on this account, it is able to take oxygen from metallic oxides placed in it; that is, to reduce them. It is, therefore, called the *reducing flame.* The extreme tip of the outer flame causes many substances to oxidize when they are heated in it, and is consequently called the *oxidizing flame.* The portion of the flame having the *highest temperature* is just above the inner cone (Fig. 35).

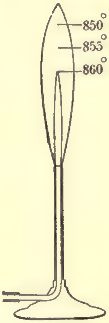


FIG. 35.

106. The Gas Range. — The burners of a gas range are modified bunsen burners. Two types of burners are used: one intended for use in boiling or frying, and the other for use during baking or broiling. Burners for use dur-

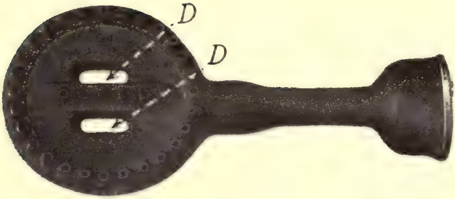


Fig. 36. — Ring Burner.

ing boiling are designed to produce a number of flames arranged in a ring or star, so as to heat large surfaces (Figs. 36 and 37).

A section of a burner connected to a gas cock is shown in Fig. 38. The "primary air" is secured by the velocity of the gas from the "spud" at *A*. This stream of gas produces a partial vacuum in the air chamber *B*, causing air to rush in through the mixer disk *F*, and mix with the gas in the throat *G*. The mixture passes to the ports *C*, where ignition takes place. The amount of air that mixes with the gas previous to ignition is regulated by

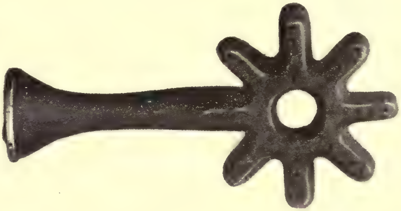


Fig. 37. — Star Burner.

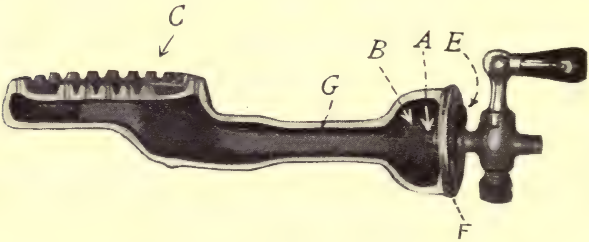


Fig. 38. — Ring Burner Section.

the adjustable mixer disk (Fig. 39). The heat from the flame causes the surrounding air to expand and rise. A supply of "secondary air" is thus continually drawn up to the flame of the burner. If too much "secondary air" is allowed to reach the flame jets, the efficiency of the burner is lowered, as a quantity of air is heated which serves no useful purpose. In the improved burner (Fig. 36), this is taken care of by making the openings *D*, *D* of such a size that they will supply sufficient secondary air to insure complete combustion, and at the same time prevent loss of efficiency by avoiding the heating of an unnecessary quantity of air. The flow of gas being constant, the air is regulated by the adjustable mixer disk (Fig. 39) which is held in place at *E* (Fig. 38) by a set screw.

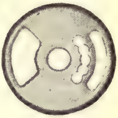


FIG. 39.

107. Efficiency of Gas Range Burners. — The most efficient flame of a gas-range burner is one in which the cross-sectional area of the inner cone is larger than that of the outer cone, and is of a blue color. If an insufficient supply of primary air is admitted through the mixer disk, yellow tips will be seen on the inner cone. If too much air is admitted, the burner will either flash back and burn at the spud, or the inner cone will be small and of a light green color. In a well-designed burner, the adjustment of the mixer disk permits the most efficient flame to be obtained under varying conditions of service.

The distance between the top of the burner and the bottom of the cooking vessel should be such that only the extreme tips of the outer cone of the flames touch the vessel. This distance for a gas range should never be less than 1¼ inches. If the distance be less, the flame is chilled by contact with the vessel and arrested combustion results. This condition may be readily detected by the garlic-like odor that is given off.

In boiling articles of food over a gas flame, it is well to

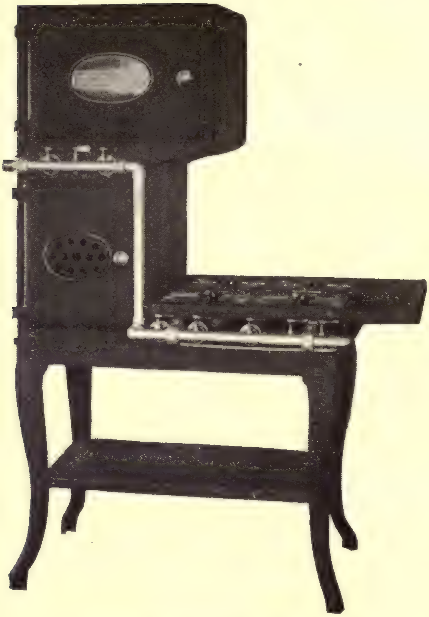


FIG. 40. — MODERN GAS STOVE.

remember that after water commences to boil, its temperature remains practically constant, no matter how much heat is applied. No increase of temperature is obtained by causing the water to evaporate (boil away) rapidly.

The burners of a gas range should never be blackened, as the ports are likely to become clogged. The burners should be removed occasionally and cleaned by boiling them in a solution of washing soda. Care must be taken to replace them in their proper positions, as each burner requires a gas way of a definite size.

108. Gas Range Oven and Broiler. — The oven and broiler are heated by several burners constructed on the same principle as those used in boiling and frying, but are of a different shape (Fig. 41).

The broiler and oven are lined for a threefold purpose:

1st. To provide a dead air space of ¼ inch around the sides and back of the range. This prevents excessive loss of heat from the oven by radiation.

2d. To provide flues to supply the secondary air to the oven burners, and to supply heated air to the oven in such a way that the heat is so distributed that the oven will bake evenly.

3d. To provide supports for the oven and broiler racks.

The oven door should always be open when the burners under the oven are lighted. When the gas is first turned on, some of it frequently enters the oven and forms a mixture with the air which may explode violently on being ignited. In heating the oven for baking, the cocks should be turned on full so as to permit the baking temperature to be quickly reached. After reaching this point, the cocks should be partly closed, as only a small amount of gas is necessary to maintain a constant temperature after the oven has once become hot. The bottom is the hottest part of the oven, and, in order to bake evenly, an article should be supported so that it will not rest on the bottom of the oven. During broiling, the broiler door should be left partly open to prevent the meat from scorching.

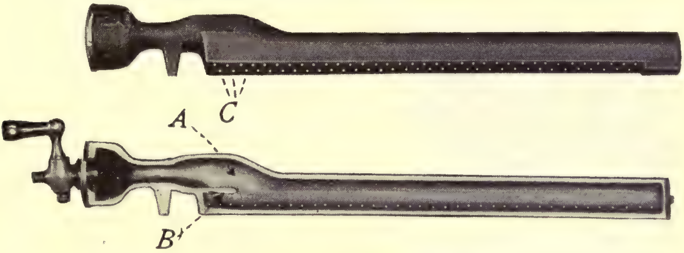


FIG. 41.—IMPROVED OVEN BURNER.

A, throat; *B*, baffle; *C*, flame jets.

109. Flue of Gas Range. — A gas stove is generally provided with a flue collar which may be connected with the chimney by a pipe, in order to dispose of the products of combustion and the heat discharged when the oven is in use. This naturally would tend to keep the kitchen cool. When the gas stove is connected with a chimney, a properly designed draft diverter should be provided, so that if there should be a back draft, the combustion of the gas burners will not be affected.

110. Gasoline Stoves. — The gasoline stove (Fig. 42) is similar in construction to the gas range, but is provided with a different kind of burner. The gasoline is stored in a tank, placed on one side of the stove and at a higher level than the burners. In the older types of gasoline stoves a little gasoline is run into a cup under the burner, and ignited. The burning gasoline heats the burner. When the burner is sufficiently hot, a valve, connecting the burner with the pipe leading from the tank, is opened. The gasoline, while passing through the hot burner, is converted into gas, which burns with a flame similar to that of the gas range.

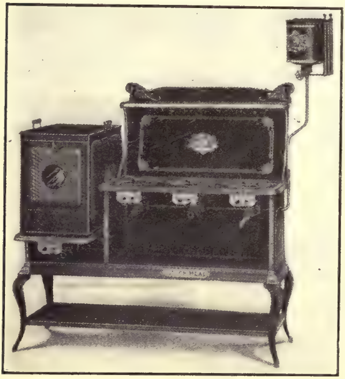


Fig. 42. — Gasoline Stove.

A more recent form of burner is shown in Fig. 43. A torch (*h*), saturated with gasoline, is lighted and slid into its casing. This causes hot air to rise through the pipe (*p*). This hot air warms the perforated evaporating tube (*a*). Gasoline is permitted to drop through the sight feed (*f*) upon the heated evaporating tube, where it turns into a heavy vapor. This mixture of gasoline vapor and air passes to the burner, where it is lighted. A small flame at the base (*e*) of the burner causes a continuous circulation through the pipes after the burner is once lighted.

Nearly all of the many accidents that have taken place during the use of gasoline stoves have been caused by filling the gasoline tank while the burner was lighted. The person in charge did not realize that gasoline is a very volatile liquid, and that a mixture of gasoline vapor and air may be highly explosive. Most of the modern gasoline stoves are made so that it is impossible to fill the tank while the burner is lighted.

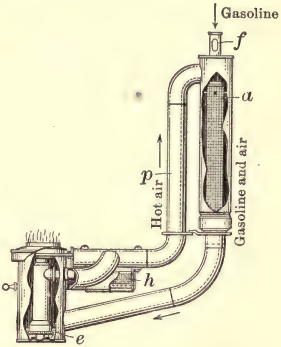


Fig. 43. — Gasoline Evaporation Burner.

SUMMARY

The **Essential Parts of a Bunsen Burner** are the base, the barrel, and the ring.

Mixture of Gas and Air. — Gas is mixed with air before combustion takes place. The quantity of gas and of air should be so regulated that a clean flame of desirable size is produced, and striking back does not occur.

The inner portion of the bunsen flame is a **Reducing Flame**, and the extreme tip is an **Oxidizing Flame**.

The **Burners of a Gas Range** are modified bunsen burners. The burner under the oven should not be lighted when the oven door is closed.

The **Gasoline Stove** is a modified gas stove. Gasoline is vaporized, and a mixture of the vapor with air is burned. The tank of a gasoline stove should never be filled while the burner is lighted.

EXERCISES

1. Name the essential parts of a bunsen burner.

2. How is (*a*) the amount of gas entering the barrel regulated? (*b*) The amount of air?

3. How does the amount of heat produced by burning a cubic foot of gas in a burner producing a colorless flame compare with that produced by a burner consuming the same amount of gas, but producing a yellow flame?

4. How do the two flames mentioned in 3 compare in size? Which produces the more intense heat per square inch of flame?

5. What are the advantages to be gained by the use of a bunsen burner?

6. Which portion of the bunsen flame has the highest temperature? Which is an oxidizing flame? Which is a reducing flame?

7. What causes a bunsen burner (*a*) to strike back; (*b*) to produce a smoky flame?

8. How may the striking back of a bunsen burner be prevented?

9. Explain how a fire may be started by a bunsen burner that has struck back.

10. Show that the burners of a gas stove are modified bunsen burners.

11. Why should the burners of a gas stove be kept clean?

12. Why is the oven of a gas stove likely to "bake too hard on the bottom"? How can this be prevented?

13. Why should the oven door of a gas range be open when the burners are lighted?

14. How does a gasoline stove resemble a gas stove?

15. Why should the tank of a gasoline stove never be filled when a burner is lighted?

16. Why is it dangerous to have gasoline fed to the burners of a stove more rapidly than it is vaporized?

17. Why should gasoline be kept in a cool place in a tightly closed vessel?

18. Under what conditions will gasoline vapor explode?

19. Give at least two reasons why it is essential that gas cocks be kept in such a condition that they can be tightly closed.

20. In boiling articles of food on a gas stove, why is it wasteful after boiling commences to burn more than enough gas to keep the water at the boiling temperature?

CHAPTER XIV

OIL AND GAS LIGHTS

111. The Candle is the simplest arrangement for artificial lighting. A candle consists of solid fat or wax molded around a braided wick of cotton thread. When the wick is lighted, the material of which the candle is composed melts, forming a small cup filled with liquid fat. The liquefied fat is drawn up the wick by capillarity, and heat converts it into vapor which burns with a flame.

A flame is simply a vapor or gas in the process of burning. A burning solid glows, but does not produce a flame. This may be illustrated by burning a piece of charcoal from which all of the volatile matter has been removed. The charcoal glows brightly, but no flame is formed.

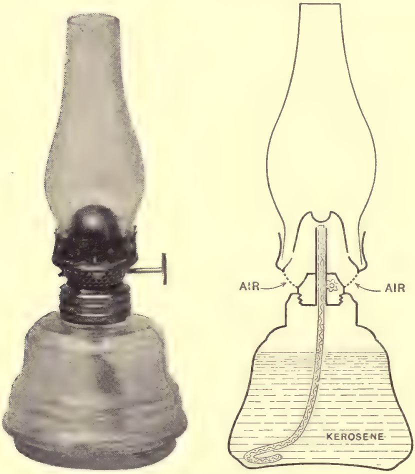


FIG. 44. — KEROSENE LAMP.

112. The Kerosene Lamp is next to the candle in simplicity of construction. The oil is drawn from the reservoir of the lamp by the capillarity of the wick, and its vapor burns with a flame.

Kerosene is a mixture of hydrocarbons. The hydrogen burns more readily than the carbon, so that the carbon would be liberated in the form of soot, if it were not for the special construction of the lamp burner and the use of a chimney to insure a proper supply of oxygen. The burner is made so that air is mixed with the kerosene vapor just before it takes fire (Fig. 44). In the "Rochester" burner, a large flame is confined in a small space by making the wick cylindrical. Air is drawn through the lamp to the inside of the flame, in addition to the air supplied to the outside of the flame (Fig. 45).

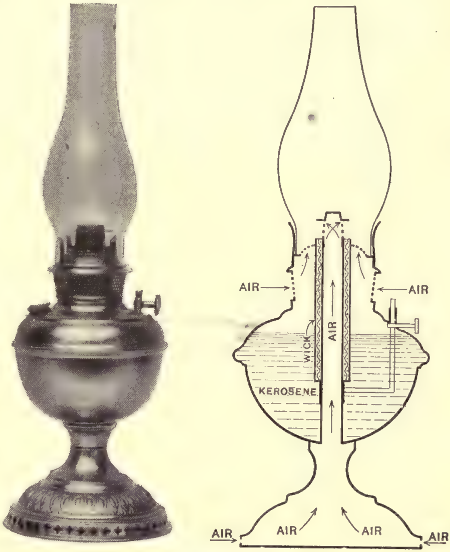


Fig. 45. — Rochester Burner.

113. The Flashing Point of an oil is the temperature at which a mixture of oil vapor and air will take fire and burn momentarily, or "flash." Most states require that the flash point of kerosene shall not be below 110° F. (44° C.).

114. Explosive Mixtures. — A little gasoline may be burned in an open dish with safety, but a mixture of gasoline vapor and air may burn so rapidly that an explosion will result. Since such substances as gasoline, benzine, and naphtha evaporate rapidly when exposed to air, they should never be used near an open flame, as the explosive mixture of their vapor and air is likely to be ignited. A kerosene of low flashing point is dangerous to use in lamps, since an explosive mixture of its vapor and air might be formed in the lamp. In the case of any gas which is used for lighting or heating, there is a range of mixtures of the gas and air which will burn explosively. Any mixture of air and hydrogen, in which the hydrogen forms from 10 % to 66 % of the whole, will explode when ignited, the most violent explosion taking place when 29 % of the mixture is hydrogen. The explosive limits of the mixture of acetylene with air are wider than the combination of other combustible gases in common use. A mixture of air and acetylene, containing from 3 % to 30 % of acetylene, will burn explosively.

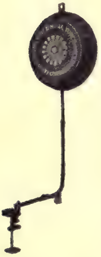


FIG. 46. — GASOLINE TORCH.

115. Gasoline Lights. — There are many devices for burning gasoline for lighting purposes. Their object is to convert the gasoline into vapor either by means of heat (Fig. 46) or by forcing air through it.

116. Gas Burners. — Two classes of gas burners are in common use, the fishtail burner (Fig. 47), and burners for use with mantles. The *fishtail burner* is a device which causes the gas to spread out in a thin sheet as it issues from the burner, so that sufficient air to burn all of the carbon is brought in contact with the gas.

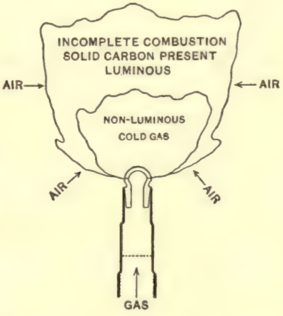


FIG. 47. — FISHTAIL FLAME.

In the case of *burners with mantles*, before the gas is burned it is mixed with sufficient air to make a mixture that will yield a colorless flame. Two forms of lamps for use with mantles are in common use: the upright lamp and the inverted lamp. The detailed construction of both upright and inverted lamps comprises the following essential features:

1. Bunsen tube.
2. Bunsen base.
3. Gas-adjustment means.
4. Air-adjustment means.
5. Mixing chamber.
6. Supports for mantle, chimneys, glassware or reflectors.

Practically the only structural difference between the upright and inverted form of lamps is the burning of the gas

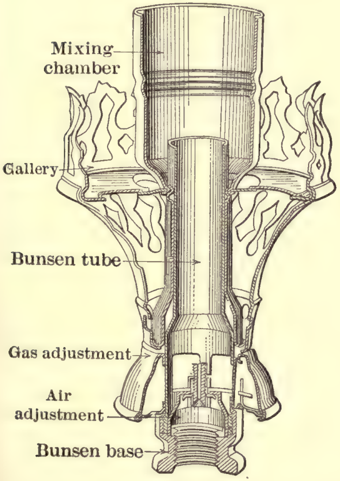

Mixing chamber
Gallery
Bunsen tube
Gas adjustment
Air adjustment
Bunsen base

FIG. 48.—UPRIGHT MANTLE BURNER.

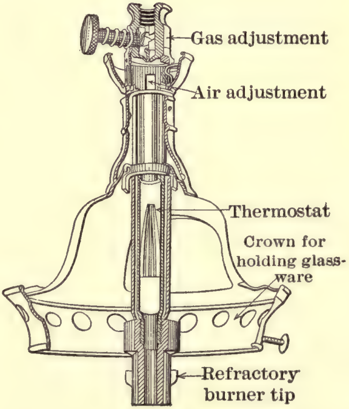

Gas adjustment
Air adjustment
Thermostat
Crown for holding glassware
Refractory burner tip

FIG. 49. — INVERTED MANTLE BURNER.

and the placing of the mantle in an upright position in the upright burner, and the burning of the gas and the placing of the mantle in a downward or inverted position in the inverted burner. The difference in lighting efficiency and distribution of light, however, is marked, the upright burner, distributing, with reflectors, only 45 % of its total light below the horizontal, while the inverted burner, without a reflector, distributes 67 % of the total light below the horizontal — the place where the light is most needed. In addition to this one fact, the inverted burner has the following advantages:

1. Improved efficiency and economy.
2. Superior decorative possibilities.
3. Greater durability and longer candle power life of the mantle.
4. Units naturally adapting themselves to all conditions and uses.

Figures 48 and 49 show respectively the cross sections of a modern upright and a modern inverted gas burner. Both of these types of lamps may be secured in various sizes, ranging in gas consumption from 1.5 cubic feet per hour to 4.5 cubic feet per hour for the upright, and from 1.5 cubic feet per hour to 9.0 cubic feet per hour for the inverted. Groupings of a number of upright or inverted mantles in one inclosing globe are made, this unit being known as the "gas arc."

117. Gas mantles are composed of mixtures of oxides of certain rare elements, chiefly thorium and cerium. The better grades of mantles are made by dipping thread made from China grass into a solution containing thorium and cerium nitrates, and then weaving the impregnated thread and making from the woven material a mantle of the required shape. Heat converts the thorium and cerium nitrates into oxides. A finished mantle contains 99 % of thorium oxide and 1 % of cerium oxide. The heat of the burning gases causes the mantle to glow brightly.

118. Gas Lighters. — With the advent of the incandescent mantle burner came the development of the pilot ignition system. This consists of a by-pass around the main gas valve, allowing a small stream of gas to pass through a tube of small interior diameter, terminating in a small flame tip located close to the mantle. The tip or pilot remains lighted when the main gas valve is closed. When this valve is opened so as to admit gas to the burner, the pilot ignites the gas and lights the lamp. These pilots consume a very small amount of gas, and afford a quick and convenient means of lighting the lamp.

In another scheme, a device on the incandescent mantle itself replaces the pilot light as a means of ignition. It consists of a small ball or pellet of platinum sponge (platinum black or very finely divided metallic platinum) which becomes heated to incandescence by the action of the hydrogen, oxygen, and carbon monoxide in the gaseous mixture, and causes the ignition of this mixture, thus lighting the lamp. The life of these pellets is very short since each ignition causes them to partially solidify.

119. Acetylene is frequently used as an illuminating gas, especially for automobile lamps. It is generated either by slowly dropping water on calcium carbide or by dropping granulated calcium carbide into water.

As acetylene is very rich in carbon, a special form of burner (Fig. 50) is required to prevent the formation of soot. Not only is the range of explosive mixtures of acetylene and air greater than that of other illuminating

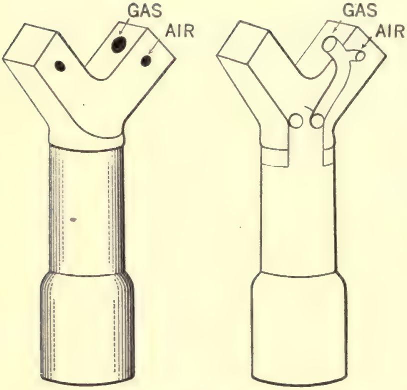


FIG. 50. — ACETYLENE BURNER.

gases, but the violence of the explosion is far greater than in the case of mixtures of other illuminating gases with air. The tremendous violence of such explosions is due not only to the great volume of the gaseous products, but also to the fact that the chemical energy latent in the acetylene molecule is suddenly liberated. It is important to keep this fact in mind when dealing with acetylene, and never use a free flame to examine acetylene apparatus. The flame (Fig. 51) produced by the acetylene burner leaves little to be desired so far as the quality of the light is concerned.

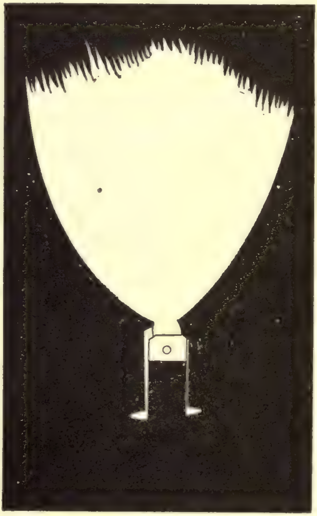
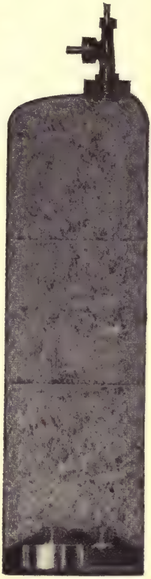


FIG. 51. — ACETYLENE FLAME.

120. Prest-O-Lite, so extensively used in automobile lamps, is acetylene dissolved in acetone. The Prest-O-Lite tank (Fig. 52) is filled with asbestos which has been soaked in acetone. On forcing acetylene into such a tank, it dissolves in the acetone. When the valve of the tank is opened, the pressure on the inside is reduced, and the acetylene passes out of solution and, by being made to pass through a pressure reducing valve, may be delivered at the lamp at any desired pressure.

121. Blaugas. — Petroleum is a more or less pure mixture of hydrocarbons. During the distillation of petroleum (Chapter XXXII), the distillate is separated into many portions and therefore the process is called *fractional distillation.* The better-known liquids obtained by the fractional distillation of petroleum are gasoline, naphtha, benzine, and kerosene. Gas oil is one of the substances obtained during the fractional distillation of petroleum, after the lighter oils just mentioned have been distilled off. When gas oil is heated to a high temperature in an apparatus free from air, it decomposes. *Oil gas* is one of the products of decomposition.



Courtesy of the *Prest-O-Lite Co.*

FIG. 52.

Herman Blau, in 1901, perfected a process for liquefying oil gas, transporting the liquid, and reconverting it into gas delivered at a pressure suitable for use in lighting and heating. Briefly stated, the process is as follows: The portion of the oil gas that liquefies at ordinary temperatures under a pressure of about 20 atmospheres is run into strong steel bottles, until the liquid fills about three fourths of each bottle. These bottles are transported to places where the gas is to be consumed. Three bottles constitute a set. The three bottles are placed in a small fireproof room, called an expander box, located outside of the building in which the gas is to be used (Fig. 53). Two of the bottles are connected with a pressure-reducing apparatus at the same time, but the valve of only one of

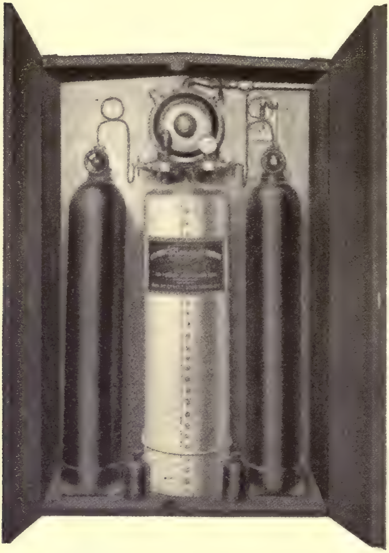


Fig. 53. — Blaugas Bottles and Expander Box.

them is opened. The liquid, drawn from the bottom of the bottle, passes to a valve which reduces the pressure so that the liquid changes into a gas. The gas is stored in a tank called an expansion tank. On leaving the expansion tank, the gas passes through a pressure regulator to the pipes of the house, where it may be used in the same way as ordinary illuminating gas. When the contents of one bottle have been consumed, the valve is closed, the valve of the second bottle opened, and the empty bottle is exchanged for the third bottle. The empty bottle is returned to the factory, where it is exchanged for a full bottle.

Blaugas, in burning, gives a bright light, with a flame of high temperature. It has a low explosion range.

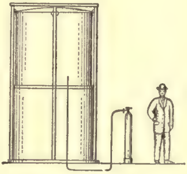


Fig. 54. — Relative Volume of Gas Liberated from Blaugas Bottle.

122. Illumination. — The following principles may be of value in determining the quality of light which should be used for illumination:

The intrinsic brightness (glare) of light within the field of vision should be reduced, so that the light will not fatigue or strain the eye.

When light strikes an object, part of the rays are absorbed by the object, part pass through it, if it is transparent or translucent, part are diffusely reflected, and part regularly reflected. This last case is worthy of further consideration. In our daily life, the results of this regular reflection from objects in the direct line of vision are serious, whether the reflection comes from the polished or glass tops of desks or tables, from the polished metal of a machine, or from the highly glazed surface of the paper in the book or magazine that one reads. This regularly reflected light strains and fatigues the eye, making it impossible for one to see well. To obviate this serious trouble, the lighting sources, where exposed to view, should be surrounded by good diffusing media of considerable area and of low intrinsic brightness.

Objects are visible because of their differences in color, and in intensity or brightness. The relative differences in intensity are largely produced by shadows. If the light in a room were perfectly diffused, there would be no shadows and the lighting might be entirely inadequate even though the intensity of illumination were correct. In order to produce shadows there must be direct light. Enough diffused light, however, must also be present to enable one to see in the shadows, but not so much that the shadows will lose their sharpness and so lose their power of making objects distinct. This point is clearly shown by places where all objects have the same color, as in flour mills; diffused light here would give results that would make the illumination not only extremely injurious to the eye, but absolutely valueless for distinguishing different objects. On the other hand, in the drafting room, where the work is done in one plane only, diffused light is required, since shadows would prove very troublesome to the draftsman.

SUMMARY

A Flame is a vapor or a gas in the process of burning. A burning solid produces no flame unless it is first vaporized.

A Candle is composed of solid fat or wax molded around a wick.

A Kerosene Lamp has a reservoir to hold the oil, a wick to carry the oil to the burner, a burner to produce a thin flame, and a chimney to increase the draft of air through the burner.

The Flash Point of an oil is the lowest temperature at which a mixture of its vapor with air will burn momentarily.

Explosive Mixtures of a combustible vapor (or gas) and air are mixtures which burn very rapidly. Their range of composition varies greatly with the kind of vapor or gas burned. Air containing 10 % to 66 % of hydrogen or with from 3 % to 30 % of acetylene, will burn explosively.

Gasoline Vapor is burned to produce light, heat, and power. It has a wide explosion range.

Gas Burners are made either to produce a thin, luminous flame, or to heat a mantle to incandescence. The mantle is composed of a mixture of 99 % of thorium oxide and 1 % of cerium oxide.

Acetylene is produced by the reaction between water and calcium carbide.

Prest-O-Lite is acetylene dissolved under pressure in acetone.

Blaugas is obtained by the destructive distillation of gas oil.

EXERCISES

1. What is a flame?

2. Does pure carbon burn with a flame? Explain.

3. What is fractional distillation?

4. What are some of the products obtained by the fractional distillation of petroleum?

5. What is the office of (*a*) the reservoir of a kerosene lamp, (*b*) the wick, (*c*) the burner, (*d*) the chimney?

6. How does the Rochester lamp differ from the ordinary lamp?

7. Define flash point.

8. What is the minimum legal flash point of kerosene?

9. Would an explosion follow setting fire to a pail of gasoline out of doors? Explain.

10. Would it be safe to allow gasoline to evaporate in a room containing a flame? Explain.

11. What is meant by "range of explosive mixtures"?

12. Will any mixture of illuminating gas and air explode when ignited? Explain.

13. What are some of the methods employed for the production of gasoline vapor for use as an illuminant?

14. What causes the luminosity of the ordinary gas flame?

15. Why should a colorless flame be used with a Welsbach burner?

16. How is acetylene made?

17. What is "Prest-O-Lite"?

18. Mention two advantages and two disadvantages in the use of acetylene as an illuminant.

19. What is "Blaugas"?

20. Mention two advantages and two disadvantages in the use of "Blaugas" as an illuminant.

CHAPTER XV

AIR AND VENTILATION

123. Physical Character of the Air. — The atmosphere may best be thought of as a gaseous ocean, resting on the earth and held in place by gravity. The air exerts a pressure of 14.7 pounds on every square inch of area at the sea level. As we ascend, the pressure becomes less, so that the exact height of the atmosphere is not known. There is, however, evidence of the existence of air as far as 200 miles from the earth. Changes in pressure, due to local heating of the air, result in winds. The barometer (Fig. 55), which measures these pressure changes, is commonly used to indicate probable changes in the weather.

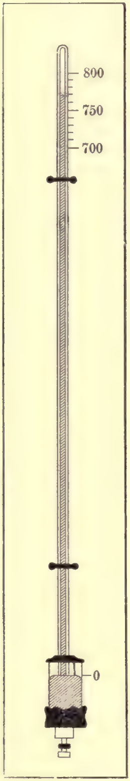


FIG. 55. — BAROMETER.

124. Composition of Air. — The important constituents of air are nitrogen, oxygen, water vapor, carbon dioxide, together with a multitude of animate and inanimate particles, constituting bacteria and dust. The proportion of oxygen and nitrogen, which together make about 99% of the atmosphere, varies to a slight extent in town and country, indoors and out of doors. The amount of water vapor present depends upon the temperature and upon the available sources of water. The percentage of carbon dioxide is affected largely by the decay of animal and vegetable matter, by the presence of numbers of people and by fires near the point where the air is collected for examination.

125. Air a Mixture. — Air is not a chemical compound, but simply a mixture of gases. The fact that its composition may vary is one proof that it is a mixture. Other proofs include the following facts. It is found that when air dissolves in water, the dissolved air contains more than one-fifth oxygen, which is the proportion in normal atmospheric air. By the application of cold and pressure, air may be liquefied and even solidified. When liquid air evaporates, the nitrogen boils off first, finally leaving nearly pure liquid oxygen, therefore the boiling point of the liquid air is not constant. If air were a compound, it would have a single definite boiling point.

126. Relation to Plant and Animal Life. — Both plant and animal life depend upon air for their continuance. Man and all other animals take oxygen from the air by means of their lungs or other breathing organs. This oxygen is carried by the blood to all the cells of the body and unites with the carbon and hydrogen of which the cells largely consist. The oxidation of the cells furnishes the heat necessary to keep the body warm and the energy which enables the muscles to do work. The products of oxidation are carbon dioxide and water:

$$\underset{\text{carbon}}{C} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2}$$

$$\underset{\text{hydrogen}}{2\,H_2} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{water}}{2\,H_2O}$$

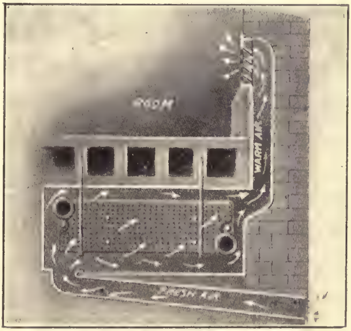
These products of cell oxidation are taken up by the blood and eliminated from the body through the lungs, skin, and kidneys. Animals, therefore, reduce the amount of oxygen in the air and increase the proportion of carbon dioxide and water vapor.

Plants breathe also, but need very little oxygen, because their movements are very slight and so a small amount of energy is needed. But plants are constantly growing and their tissues also consist largely of carbon and hydrogen. All the carbon in plants comes from the carbon dioxide in the air. This is absorbed by the leaves and in them unites with the water taken up by the roots, finally forming sugar, starch, and wood. By this process, the oxygen of the absorbed carbon dioxide is liberated and returned to the air. Plants, therefore, reduce the percentage of carbon dioxide in the air and increase the percentage of oxygen. Decay, fermentation, and fires contribute largely to the carbon dioxide in the air. The ease with which gases diffuse and the action of the winds greatly assist in maintaining the uniformity of the atmosphere. Thus we see that natural agencies, working together, tend to keep the proportion of oxygen and carbon dioxide in the air constant.

127. Ventilation. — In buildings, the balance of oxygen and carbon dioxide cannot be maintained without artificial aid; hence ventilation, which is the substitution of fresh air for contaminated air, is necessary. Pure air contains 3 to 4 parts of carbon dioxide in 10,000; when this is increased in rooms to 30 or 40 parts in 10,000, with a corresponding increase in water vapor and other emanations of the body, the air becomes close; then breathing is no longer comfortable. When we consider that about 5% of the air expelled from the lungs is carbon dioxide, and that lamps and gas flames return to the air a volume of carbon dioxide equal to the volume of oxygen consumed, it is not surprising that about 3000 cubic feet of fresh air per hour for each person in a room are required for health.

Rooms are not perfectly closed boxes, and some fresh air finds its way in through cracks and when doors are opened. But such ventilation is not sufficient, particularly when a number of people are in the same room. Open fireplaces aid greatly in the ventilation of rooms, as fresh air finds its way in through all openings and cracks more rapidly, to force the lighter hot air up the chimney. When the fire is not burning, however, cold air tends to come down the chimney, pocketing, near the ceiling, the impure heated air already in the room and so failing to produce a circulation of fresh air. It is well to keep in mind that exhaled air from the lungs and the waste gases from lamps and gas burners rise because their temperature makes them lighter, although the carbon dioxide in them is heavier than pure air at the same temperature.

The amount of leakage around windows and doors and through the walls of a room is sufficient to change the air about once an hour in winter weather. To secure additional ventilation, fresh air must be admitted and foul air allowed to escape, without causing drafts. When a house is heated by a properly designed and well-managed hot-air furnace, this does much to promote circulation, and has the additional advantage of warming the incoming air. Houses otherwise heated secure a considerable amount of fresh air by the opening of the outside door as people pass in and out. Usually



Courtesy of *The Scientific American.*

FIG. 56. — INDIRECT HEATING SYSTEM.

this is not enough. Systems of combined heating and ventilation have been devised in which hot water or steam radiators are placed in boxes provided with an inlet for fresh air from outdoors, and an outlet for discharging the heated fresh air into the room (Fig. 56). This method is efficient as far as furnishing properly warmed fresh air is concerned, but is wasteful of fuel in times of high winds and cold weather.

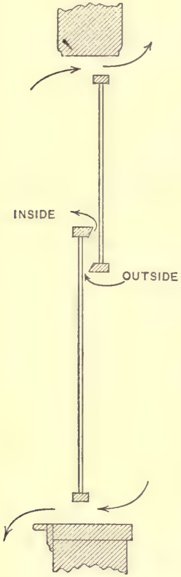


FIG. 57. — AIR CURRENTS AT AN OPEN WINDOW.

When windows are used for ventilation, they should be opened at both top and bottom, if the weather permits, or in any case at the top. The cold air will force its way in through the bottom opening, or up between the sashes, and drive out the warm, foul air easily and directly through the opening at the top (Fig. 57). If the window is opened at the bottom as well as at the top, drafts should be avoided by deflecting the incoming cold air, so that it will flow up the sash a little way, and not blow horizontally into the room. The windows of sleeping rooms should always be opened top and bottom, the amount of opening being suited to weather conditions.

Halls, churches, schools, theaters, tenement and apartment houses, and all other places where a large number of people gather in a comparatively small space, require special ventilation. Fresh warmed air should be distributed to each room through a definite flue and the foul air removed through another flue. Positive means of securing circulation, such as a blower to drive the fresh air over heating coils and into the rooms, and another blower to draw the foul air out of the rooms, should be adopted in schools and public buildings.

128. Nitrogen. — Nitrogen, comprising nearly four fifths of the air, is the largest constituent of the atmosphere. It is an inert gas, that is, it does not support combustion and does not readily unite with other elements. Nitrogen dilutes the oxygen in the air and thus lessens the speed of oxidation. Nitrogen cannot be directly assimilated by animals nor by plants in general, yet nitrogen is an important constituent of all living bodies. Protoplasm, the essential substance in living tissues, is a very complex compound containing nitrogen. Meat and the white of egg are examples of substances particularly rich in nitrogen. Animals are compelled to depend upon plants or upon the flesh of other animals for their nitrogen compounds. Plants, however, can manufacture protoplasm in their cells, taking simple nitrogen compounds from the soil through their sap. Thus, in time, the nitrogen of the soil becomes exhausted, and nitrates or other compounds of nitrogen must be used as fertilizers (see Chap. XLV). Nitrogen is also an important constituent of explosives.

Associated with nitrogen and distinguished from it only a few years ago, are other gases resembling nitrogen. Argon is the chief of these inert gases, which together form about 1 % of the air. They form no compounds and seem to be without chemical activity.

129. Carbon Dioxide. — The presence and proportion of carbon dioxide in the air has already been mentioned. It is an odorless gas, about one and a half times as heavy as air. The most marked characteristic of carbon dioxide is that it will neither support combustion nor life. Where ventilation does not take place readily, as in caves and wells, the carbon dioxide formed from decay or as a result of decomposition going on in the earth, sometimes accumulates, displacing the normal air. Before entering such places for any purpose one should test them with a burning candle. If the candle continues to burn brightly, it is safe to enter; otherwise suffocation might result.

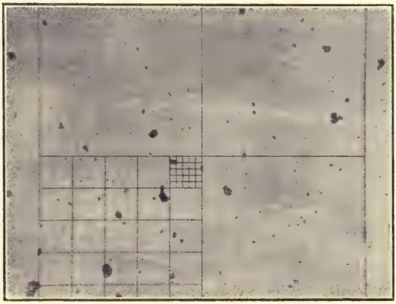
The usual test for the purity of air is to determine the percentage of carbon dioxide in it. This is because the amount of carbon dioxide produced by breathing or by fires serves as an index to the amount of other impurities, which are present in smaller amounts and are more difficult to determine. The unpleasant effects in crowded rooms of air containing less than 1% of carbon dioxide is probably due in large measure to the presence of these other impurities and of water vapor. This is shown by the fact that in factories where carbon dioxide is made for charging soda fountains and mineral water, the air may contain much more than 1% of carbon dioxide without any unpleasant effect being experienced.

130. Water Vapor. — Water vapor is always present in the air, even in desert climates, but the proportion which air may contain before becoming saturated depends upon the temperature. While air at 32° F. can hold less than 5 grams of water to the cubic meter without precipitating it in the form of rain or snow, air at 60° F. can hold nearly 13 grams, and air at 90° F. about 34 grams of water vapor per cubic meter before becoming saturated. The cloud of water dust seen when we exhale on a cold day is due to the fact that, while the air from the lungs is not saturated at the temperature of the body, it is more than saturated at the temperature of the surrounding atmosphere. The frost on windows is caused in a similar manner.

The amount of water vapor present in the air reaches the saturation point only when it is rainy or foggy. On a clear day the proportion may be only 30 or 40 % of the amount needed for saturation. The evaporation of perspiration from the skin depends not only on the temperature of the air, but also on the amount of vapor already present in the air. When the atmosphere is nearly saturated with water, evaporation is checked, and we become uncomfortable. This probably accounts largely for the discomfort of crowded rooms, as noted above. On the other hand, if there is very little vapor in the air, evaporation is too rapid. This is the usual condition of buildings heated by any of the ordinary methods; their climate is that of the desert. This may be remedied by providing a supply of water so located that it may readily evaporate into the air supply of the room.

131. Relative Humidity. — The quotient obtained by dividing the amount of vapor actually present by the amount necessary for saturation at the observed temperature, is the *relative humidity*. A humidity of about 60 % is nearly right for comfort. On a hot, muggy day the relative humidity is very high, evaporation is checked, and we feel uncomfortable and out of sorts. The bracing quality of a cool, dry day is due largely to the low relative humidity.

132. Dust and Bacteria. — In addition to the gaseous substances already discussed, the air always contains great numbers of solid particles small enough to be blown about by the winds, and so small that they settle very slowly, even through perfectly still air. The larger ones can be both seen and felt as dust particles; smaller ones are the motes which show the path of a beam of light through a room; and still smaller ones are revealed when an undusted object is examined with a microscope. The name "dust" is usually applied to all such particles, but it might better be limited to mineral particles and dead organic matter. The number of particles of dust in a cubic inch may range from 2000 in the open country to 30,000,000 in an occupied room. A very large proportion of the latter number are not dead matter, but are the tiny living organisms called bacteria, germs, microbes, etc. These are usually single-celled, living bodies, capable of reproducing themselves with enormous rapidity when they find suitable conditions. These conditions include warmth, moisture, and suitable food material. Fermentation and decay are produced by the action of bacteria, since animal and plant material, living or dead, affords the proper conditions for their growth and reproduction.

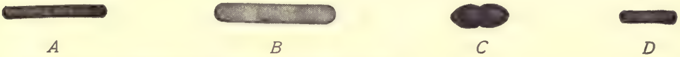


Magnified 40 diameters.

FIG. 58. — PHOTOMICROGRAPH OF DUST IN AIR.

In the case of many contagious diseases, the particular variety of bacteria associated with the disease has been identified and the treatment adopted is designed to destroy these bacteria. Many forms of bacteria, such as that causing consumption, may dry up and remain without apparent life for long periods, and then become active as soon as the proper conditions are provided.

It will be seen, from this very brief statement of the constitution of dust, how important it is to avoid breathing more dusty air than we can possibly help. Every precaution should be taken in the case of germ diseases to prevent the escape of the germs and so cause the disease to spread. A sheet kept moist with a disinfectant solution — that is, one which will kill injurious bacteria — and hung before the door of a sick room, helps very much to prevent the spread of germs through the air to other rooms. Fumigation of a room in which there has been a case of contagious disease by gaseous disinfectants, such as formaldehyde, or sulphur dioxide, is for the purpose of destroying the germs in the air as well as those which have settled.



Courtesy of the *American Museum of Natural History.*

FIG. 59. — BACTERIA FOUND IN AIR (MAGNIFIED 4000 DIAMETERS).

A, Bacillus of tuberculosis; *B*, Bacillus of diphtheria; *C*, Diplococcus of pneumonia; *D*, Bacillus of influenza.

133. Other Constituents of Air. — Other gases which are present in the air in small amounts are nitric acid, ammonia, and ozone. The *nitric acid* is formed by the solution of nitrogen oxides in the moisture of the upper atmosphere. These nitrogen oxides are formed by the combination of nitrogen and oxygen when the air is highly heated by the passage of a flash of lightning. The *ammonia* is chiefly the result of the decomposition of organic matter containing nitrogen; its odor is noticeable in stables and other places where such decomposition is taking place. By diffusion, ammonia is distributed throughout the atmosphere. Both ammonia and nitric acid are washed out of the air during rain storms and so help to restore nitrogen to the soil.

Ozone is a more active form of oxygen. It is a gas with a penetrating odor, and is always formed when electric sparks are passing through the air. During thunder storms it is produced in considerable quantities and probably contributes to the invigorating quality of the air immediately after a storm. This quality of air is also due to the fact that the rain washes the dust and smoke out of the air, leaving it clearer and more transparent. Ozone is known to be a good bleaching agent and disinfectant, and the bleaching of cloth spread on the grass is commonly believed to be caused by ozone. Ozone is also found where waves are beaten into surf on the shore and it contributes to the invigorating quality of sea air. Other gases and impurities are present in the air in certain localities, but they are only found locally and so we need not consider them.

SUMMARY

The Chief Constituents of air are nitrogen and oxygen, mixed in the proportion of about 4 parts of nitrogen to 1 of oxygen. Air is not a chemical compound. Water vapor and carbon dioxide are other important constituents of air.

Animals, in breathing, take oxygen from the air and give carbon dioxide to it.

Plants, in the formation of starch, take carbon dioxide from the air and give oxygen to it.

Air in Rooms must be constantly renewed, in order to remove the waste gases exhaled and to renew the supply of available oxygen. Good ventilation requires constant change of air, without draughts.

Nitrogen is a gas which does not react readily with other elements. It is an essential constituent of all living bodies.

Carbon Dioxide will support neither combustion nor life. The percentage of carbon dioxide in air serves as an index of the total impurities present.

The percentage of **Water Vapor** in air is constantly changing, and affects the climate and also human comfort.

Dust in the air always contains bacteria, and so every precaution should be taken to avoid breathing dust and to protect food from it.

Other constituents of the air include nitric acid, ammonia, and ozone.

EXERCISES

1. Name four constituents of air and state the importance of each to man.

2. Give two proofs that air is a mixture and not a compound.

3. Show how plants and animals depend on each other for existence.

4. Why is oxygen necessary for animal life?

5. State, with reasons, the best way of ventilating your sleeping room.

6. Discuss fireplaces as a means of ventilation.

7. Would a person die if shut up in a room with the doors and windows closed? Explain.

8. Why do schools require more systematic ventilation than houses?

9. Compare nitrogen with oxygen in its chemical activity. In its importance to man.

10. Why are nitrogen compounds of great importance in fertilizers?

11. Why are we more uncomfortable when the humidity is high than when it is low?

12. Why is the air chamber of a hot-air furnace provided with a pan for water?

13. Show the relation of bacteria to dust and to disease.

14. Why is vacuum cleaning more sanitary than sweeping?

15. What is ozone? How is it produced? What are its uses?

16. Compare steam heat and furnace heat as aids to the ventilation of a house. How do these two systems affect the humidity of the air in the rooms?

CHAPTER XVI

CHEMICAL PURIFICATION

134. Chemical Purity. — Granulated sugar and starch are two substances which come into the household in a high state of purity. Nearly everything else that we see or use is a mixture which bears the name of the dominant material, but which contains many others. The minor constituents are usually not objectionable, and are allowed to remain because the process of removing them is too expensive. In the case of sugar, although the natural impurities that are present in the first stages of the manufacturing process would do no great harm, we get the article in a pure state because the public likes it to be crystalline in appearance. Furthermore, the process of purification is not very expensive.

For much chemical work, a state of purity comparable to that of starch and of sugar is desirable ; it is essential in all that involves analysis or a study of properties. Hence the processes of purification are an important part of a chemist's knowledge. High degrees of purity are difficult to obtain, and absolute purity is wholly a theoretical matter. Even water has never, in all probability, been obtained in a state of perfect purity.

135. Purification of Gases. — As a rule, impurities are removed from gaseous mixtures by means of chemical action. The gases are passed through liquids or over solids that will react with the impurity. Hydrogen sulphide is removed from illuminating gas by passing it over moist iron oxide. Carbon dioxide can be removed from other gases by passing the mixture through a solution of potassium hydroxide, or over sticks of the solid substance. Water vapor is absorbed by passing the moist gas through concentrated sulphuric acid, or over lumps of anhydrous calcium chloride.

Pure, dry hydrogen is obtained by passing the gas from the generator (Fig. 60, *a*) through an acid solution of potassium permanganate (*b*) to remove hydrogen sulphide, and through concentrated sulphuric acid (*c* and *d*) to remove water vapor.

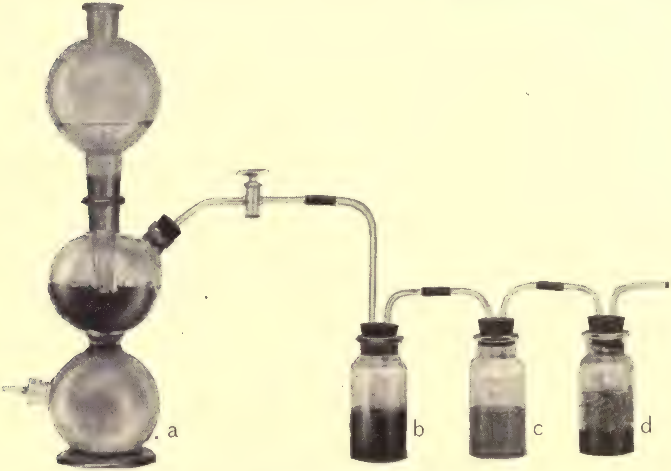


FIG. 60. — PURIFICATION OF HYDROGEN.

136. Purification of Liquids by Distillation. — If a liquid contains a dissolved impurity, whether the latter be a solid, liquid, or gas, the process of boiling, or of boiling and condensation, is usually employed to bring about a separation. Gases are less soluble in hot than in cold liquids, and continued boiling will therefore drive out a gas from a liquid solvent.

If the dissolved impurity is itself a liquid, the solution is boiled and the gases that come off are led through a tube that is surrounded by cold water, whereby they are *condensed* and again become liquids (Fig. 61). This double process is called *distillation*. Since every chemical compound that will endure distillation without decomposition has its own definite and constant boiling point, the constituents of the liquid mixture *tend* to come off at different temperatures during the heating. The boiling begins at a temperature near that required for the boiling of the constituent having the lowest boiling point, and the condensed liquid will at first consist mostly of this more volatile substance. In distilling a mixture of alcohol and water, for example, the boiling begins near 80°, and the

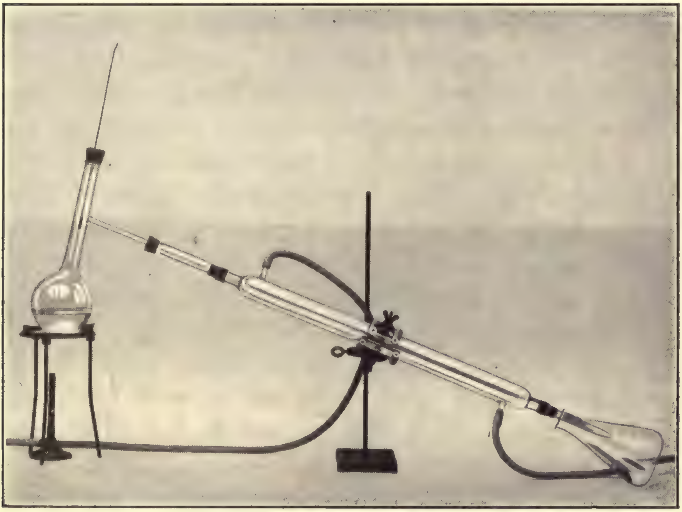


FIG. 61. — LABORATORY DISTILLATION.

temperature gradually rises to over 100° C. The first part of the liquid that condenses, the *distillate*, is largely alcohol, but it contains some water; the last part of the distillate is water containing a little alcohol.

Using this principle, a mixture of two liquids can be separated to a greater or less extent. If the boiling points lie close together, as in the case of alcohol and water, repeated distillation is necessary, and a complete separation cannot be effected by distillation alone. If the boiling points lie far apart, the separation is easier. There are a few cases where a mixture will boil at a constant temperature, provided the pressure remains the same, and will give a distillate of definite composition, for example, a mixture of acetic acid and water, or a mixture of nitric acid and water.

When liquids contain dissolved solids, the liquid can almost always be distilled and a nearly perfect separation easily effected.

In many kinds of chemical manufacturing, distillation is an essential part of the process and is carried out on a very large scale. By such a process, we get from crude petroleum many different products such as naphtha, gasoline, kerosene, and lubricating oils.

137. Purification of Liquids by Freezing. — When a solution is frozen, the solvent separates as a comparatively pure substance. Hence, if a liquid mixture is cooled to the freezing point of the solvent, as the latter gradually solidifies, the impurity will remain in the unfrozen part of the solution. When brine freezes, the ice that forms is practically free from salt. This process often affords a convenient means of purification.

138. Purification of Solids. — Distillation may also be used as a means of purifying solids, provided the solid does not change chemically in being heated to its boiling point. Many solids are commercially refined in this way. Among them are sulphur, camphor, iodine, and even the metal zinc. The process is called *sublimation* when the condensed substance is deposited as a solid. More commonly, in the purification of solids, other processes are utilized that depend upon solution, washing, precipitation, filtration, and crystallization. All chemical manufacturing involves a large amount of this work.

139. Washing and Filtration. — Filtration may be one of two operations: (*a*) the straining out of a solid from a liquid by passing the liquid through a porous substance such as paper or cloth, the solid remaining on the filtering surface; (*b*) passing a solution through a thick layer of powdered material, such as animal charcoal, which will absorb impurities that are in solution. *Washing* is practically a filtration in which the solid substance to be purified is placed on a porous substance, and the impurities washed out by treating with a suitable liquid, which drains through, carrying the impurities with it (Fig. 62). The first operation in the refining of raw sugar is a pro-

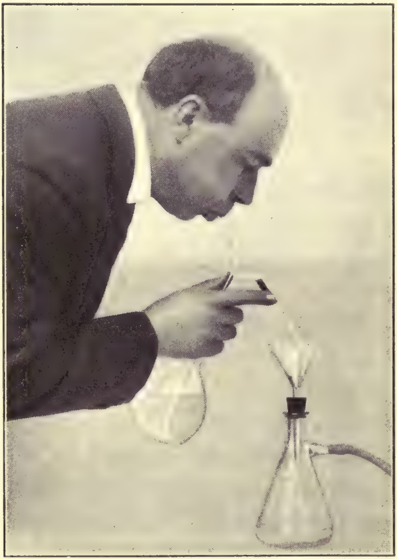


FIG. 62. — WASHING A PRECIPITATE ON A SUCTION FILTER.

cess of this sort. In this case, and in many other manufacturing operations, the process is greatly hastened by the use of centrifugal filters. These are large pans with many fine perforations in the sides (Fig. 63, *b*), capable of being rotated in a horizontal plane with great velocity. The liquid part of any mixture that is put in them is thrown off with great rapidity and completeness by centrifugal action. A later operation in the purification of sugar consists in passing it in solution through a very thick layer of bone charcoal. This represents the second kind of filtration described above. Impurities that would give the sugar a brown color are absorbed by the charcoal, and the solution comes through nearly colorless.

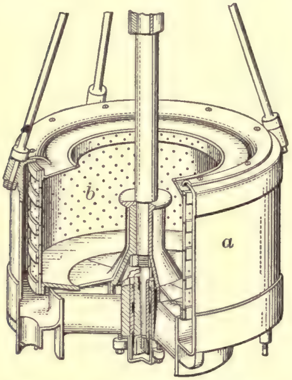


Fig. 63.—Centrifugal Filter. *a*, outer drum; *b*, perforated drum.

140. Precipitation. — This operation can often be used as a means of purification. When an insoluble substance is formed within a solution by either physical or chemical action, it separates as a definite chemical compound, and other substances remain in solution. The precipitated material has merely to be filtered off and washed, to be obtained in a high state of purity. An application of this principle will give a form of common salt so pure that it will not deliquesce. Ordinary salt is dissolved in the least quantity of water that will suffice, and hydrogen chloride is added. The sodium chloride, being much less soluble in a solution of hydrochloric acid than in water, separates as crystals. The disturbing impurity, magnesium chloride, is left in the solution.

141. Crystallization. — Crystallization is a term used to indicate a kind of slow precipitation in which the substance that separates assumes a regular and symmetrical form (Fig. 64). It is brought about by a change in the physical condition of the solvent, usually a lowering of its temperature or a diminution of its volume. Impurities, if present, remain in the solvent, as does a part of the solute. This remaining liquid portion is called the mother liquor.

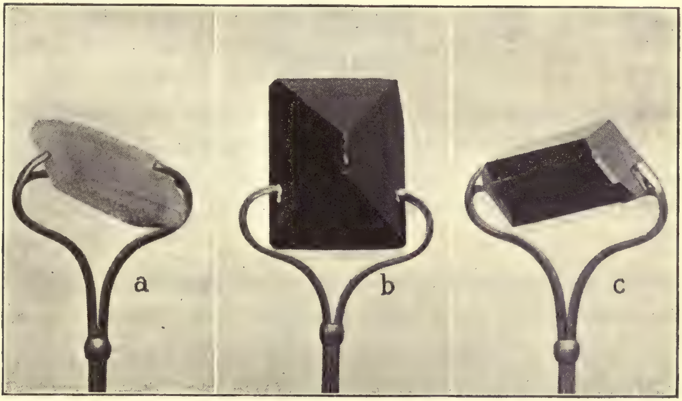


FIG. 64. — TYPICAL CRYSTALS.

a, K_2SO_4; *b*, $K_2SO_4\,Cr_2(SO_4)_3.24\,H_2O$; *c*, $CuSO_4.5\,H_2O$.

For purposes of purification, it is desirable to have the individual crystals as small as possible. This result is obtained by stirring the mixture thoroughly while the crystals are forming. There is always a tendency for the crystal to retain within itself a certain amount of mother liquor; but if the crystal is small, there is less chance of this contamination. Since it cannot be altogether avoided, a single crystallization may not give a very high grade of purity. As with the separation of liquids by distillation, several repetitions of the process are frequently employed, and we speak of the process as *recrystallization*. After the crystals are formed, they are separated from the mother liquor by filtration, and perhaps washed with a small quantity of the pure solvent. The final operations in the purification of sugar are those of recrystallization.

SUMMARY

Chemical Compounds, even tolerably free from other substances, are not easily prepared. High degrees of purity are secured only after repeated operations, and absolute purity does not exist. Sugar and starch are two substances that come into the house in a high state of purity.

Gases are purified by bringing them into contact with liquids or with solids that will react chemically with the impurities.

Distillation is a process that includes two operations: first, the converting of liquids or solids into gases by heat; second, the cooling of these gases until they again assume a liquid or solid form. If the cooled substance is deposited immediately as a solid, the process is termed **sublimation.**

Distillation and sublimation are important methods of purification. The principle underlying the methods is that different chemical compounds are converted into gases, each at its own definite and characteristic temperature. Mixtures of mutually soluble liquids do not boil exactly according to this principle; the boiling begins at a temperature near that required for the boiling of the constituent having the lower boiling point, and in most cases the temperature then rises gradually to or above that required for the constituent having the higher boiling point. The substance that comes off (the *distillate*) is a mixture of the two liquids in varying proportion.

Repeated distillation is necessary to separate a mixture of such liquids.

Gases are less soluble in hot than in cold liquids.

When a solvent freezes, dissolved substances that are present are precipitated, or remain dissolved in the unfrozen part of the solution.

Filtration and Washing are used to separate insoluble solids from soluble ones. Filtration also includes purification by absorption of soluble impurities from solutions as, for example, decolorization of sugar sirup by charcoal. Centrifugal filters permit very rapid filtration and washing.

Precipitation occurs when an insoluble solid is formed within a solution, or when a condition of insolubility for a substance has been established in a solution. Such a precipitated substance can be obtained in a pure state by filtering it from the solution and washing.

Crystallization is a kind of precipitation in which the solid separates more or less slowly and in doing so assumes a regular geometric form. It may be used as a means of purification for the same reasons that precipitation may be so used. Repetitions of the process are necessary to secure any high degree of purity.

EXERCISES

1. Why is not chemical purity necessary for most purposes? Distinguish between water that is chemically pure, and water that is hygienically pure.

2. How would you remove hydrogen sulphide (a gas) from water in which it was dissolved? Explain.

3. How could you separate sugar from earth or sand and save the sugar?

4. How would you separate oxygen from air so as to obtain nitrogen?

5. How would you obtain dry air for a chemical experiment?

6. Define distillation, sublimation, crystallization, recrystallization, and filtration.

7. How would you obtain pure water and pure salt from brine?

8. Describe what happens when a mixture of alcohol and water is distilled.

9. How could gasoline that had been used to clean clothing be recovered in a pure state? What sources of danger attend this operation?

10. If a solution containing sodium chloride, water, and ammonia gas were distilled, what would happen?

11. In the cold parts of Russia, salt is obtained from sea water by freezing. What principle is involved? How would the operation be carried out?

12. Describe the action of centrifugal filters.

13. Why is bone charcoal used in the purification of sugar?

14. Which would taste salter, sea water or water resulting from the melting of sea ice? Why?

15. Define precipitation. Why can it be used as a means of purification?

16. How could you obtain pure sodium chloride from a solution that also contained a little potassium nitrate?

17. How would you proceed in order to get large crystals from a solution? Small ones? Which would be better if you were using crystallization as a means of purification?

CHAPTER XVII

WATER

142. Value of Water. — Every one understanding the life processes of plants and animals fully realizes the importance of water. With the increase of population, the struggle to secure a sufficient supply of pure and wholesome water has become a most vital problem of the present day. Only within the last twenty years have American communities realized the value of pure water in conserving the health of the people and in promoting their prosperity.

143. Sources of Water. — The sources of water supply may be classed in two divisions, *surface waters* and *ground waters.* The surface waters include the rain collected from roofs, river waters, water in natural lakes, and the water collected from watersheds in reservoirs. Ground waters comprise the waters of springs, wells, and underground chambers or galleries. The source selected for a town or city supply depends mainly on two factors, — the quantity and the quality of the water. The quality is determined by substances either dissolved or suspended in the water.

144. Content of Natural Waters. — As a result of the intimate association with life and other natural processes, surface and ground waters contain a wide variety of substances. These may be roughly classified according to their origin, as organic and inorganic. The organic materials are derived from animal and vegetable life. After the death of living matter, bacterial processes of putrefaction and decay disintegrate the tissues. The products of decomposition either blend with the soil already formed, or escape into the air as gaseous substances, such as ammonia, nitrogen, or carbon dioxide. As water mingles with the soil, it not only takes up the products of decomposition of organic matter, but also countless numbers of bacteria of various kinds. It is usually these small forms of life, and not the organic compounds, that render water unfit for human use.

The inorganic materials of natural waters consist mainly of soluble salts, such as carbonates, chlorides, and sulphates. They are chiefly compounds of calcium, magnesium, sodium, potassium, and iron. These compounds are dissolved or taken into suspension as the waters run over the ground, percolate through the soil, or make their way through rocky strata.

The nitrates and nitrites found in natural waters owe their formation to the nitrifying organisms in the soil. Dissolved oxygen is another substance in natural waters and is important for the part that it plays in their purification.

Although simple tests are available for the detection of the various contents of natural waters, accurate quantitative determinations and their interpretation require a skilled chemist.

The following analysis gives some idea of the substances contained in natural waters. Although the number of dissolved substances may be large, such waters are actually very dilute solutions, so dilute in fact, that the amounts of the dissolved substances are expressed in parts per million by weight.

ANALYSIS OF CROTON WATER, NEW YORK CITY

Appearance	Very slightly turbid
Color	Light yellow brown
Odor (heated to 100° F.)	Slightly marshy
Chlorine	2.100 parts per million
Equivalent to sodium chloride	3.460 parts per million
Phosphates	0.000 parts per million
Nitrogen in nitrates	0.250 parts per million
Nitrogen in nitrites	0.000 parts per million
Free ammonia	0.015 parts per million
Albuminoid ammonia	0.170 parts per million
Hardness equivalent to calcium carbonate, before boiling	37.500 parts per million
Hardness equivalent to calcium carbonate, after boiling	33.300 parts per million
Organic and volatile matter (loss on ignition)	15.000 parts per million
Mineral matter	66.000 parts per million
Total solids	81.000 parts per million

145. Pure and Wholesome Water. — The value of a water intended for drinking does not depend upon the number, but rather upon the kind of substances that it contains, and upon certain physical characteristics. A satisfactory water should be colorless, should be free from turbidity, objectionable tastes and odors, and should not contain any substances, or forms of life dangerous to health. Moreover, its temperature should fall within the range at which water is palatable. Such a water will be wholesome and pure in a sanitary sense, although not necessarily pure according to the chemist's idea. A knowledge of the requisites for wholesome water may best be gained by a consideration of the factors upon which these desirable qualities depend.

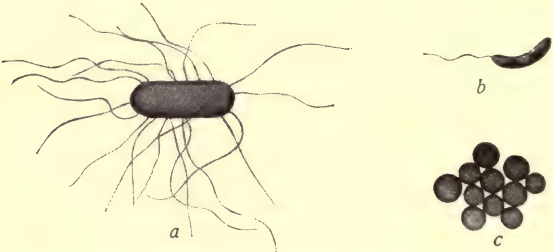
146. Color of Water. — Ground waters are usually colorless, while surface waters often vary from light yellow to dark brown. The color is usually due to organic material, which is dissolved as the water drains through swampy or forest areas. Occasionally the water supply of a city may become discolored from the surface washings of the reservoir area due to a heavy rain. Many colored waters are wholesome, but are unattractive and therefore undesirable for public water supplies. In the reports of sanitary chemists, the color of water means color due to dissolved substances and should not be confused with color due to turbidity.

147. Turbidity. — The turbidity of water is due to particles of suspended matter of various kinds, sand and particularly clay being the most frequent materials. A water may contain a considerable amount of sand and still look clean, while a very small amount of clay may produce very turbid water. The latter waters owe their turbidity to iron compounds changing from ferrous to ferric salts. At certain seasons of the year, several forms of plant life (algæ and diatoms) grow with great rapidity, and as rapidly disintegrate, clouding the water with dead and dying plant tissues. Organic material from the soil often causes waters to become turbid, especially when the material is in an active state of decomposition. The *iron bacterium*, which thrives in the presence of iron compounds and organic matter, makes many waters turbid. The turbidity due to suspended clay or sand, although undesirable, is far less likely to make a water unwholesome than a turbidity due to suspended organic matter in a state of decomposition.

148. Odor and Taste. — The usual agreeable odor and taste of water is due mainly to dissolved oxygen and carbon dioxide. Water without these dissolved gases tastes flat. Iron or sulphur compounds, and certain other salts, give some waters a pronounced odor and taste. Some spring waters have an earthy odor, due to volatile substances absorbed from the soil. Occasionally the odor and taste are due to putrefying organic material, but more frequently are due to oils formed in the cells of certain organisms. A diatom, *asterionella*, gives an aromatic odor. The blue-green algæ give grassy odors, — one variety, *anabœna*, mixed with water gives it a taste like green corn. Minute and lower forms of animal life are usually responsible for fishy tastes and odors.

149. Transmission of Disease by Water. — The disastrous effects resulting from the use of impure water were clearly shown in the southern camps of our soldiers in the Spanish war of 1898. Neglect of sanitary precautions led to a greater loss of life and health than that due to the military operations. Six years later, Japan, profiting by the advance in sanitary science, sent its chemists and sanitary engineers ahead of the main army to test the water supplies and indicate the wholesome ones. When the army was in camp, the enforcements of strict sanitary regulations prevented the contamination of the sources of water. As a result, the Japanese army was free to a marked degree from the diseases that had weakened many armies in earlier wars. Too often the value of pure water has been demonstrated to towns and cities by disastrous epidemics due unquestionably to polluted water supplies.

The transmission of disease by water depends upon (1) the introduction of the disease germs into the water, usually by sewage, (2) the survival and maintenance of the vitality of the germs under favorable conditions until they are taken into the system. Fortunately the conditions prevailing in natural waters result in the death of most disease germs. Accordingly the number of water-borne diseases is not large, but, on the other hand, they are among the most deadly, as they give rise to serious affections of the intestinal tract. Asiatic cholera, typhoid fever, dysentery, and cholera infantum are known to be transmitted by water. In fact, severe epidemics of these diseases have been traced to the use of contaminated water.



Courtesy of *The American Museum of Natural History.*

FIG. 65. — WATER-BORNE BACTERIA.

a, Bacillus of typhoid fever; *b*, Spirillum of Asiatic cholera; *c*, Staphylococci. (Magnified 4000 diameters.)

The cholera epidemic of 1892 in Hamburg and Altona strikingly demonstrated that the spread of the disease was mainly due to impure river water. These two cities are practically one, as no natural boundary separates them. Hamburg took its water from the river Elbe and did not filter it, while Altona, with water from the same river, and still more contaminated, used an efficient system of sand filtration. The following table tells its own story:

CITY	POPULATION	CASES OF CHOLERA	CHOLERA DEATHS	DEATH RATE PER 10,000
Hamburg . .	600,000	17,000	8,600	134.0
Altona . . .	150,000	500	300	21.3

One block in Hamburg which happened to be supplied with Altona water was free from the disease, while the neighbors across the street paid the penalty for drinking the impure Hamburg water. No doubt many of the cholera cases of Altona were contracted by the Altona people while at their daily work in Hamburg.

The following table shows the decrease in typhoid in this country concurrent with the increasing number of filtered public water supplies. The statistics are for twelve states, all the New England States, New York, New Jersey, Maryland, Michigan, Minnesota, and California.

AVERAGE TYPHOID DEATH RATE PER 100,000[1]

1880	55
1885	46
1890	36
1895	28
1900	23
1905	21
1910	19

Instance after instance can be cited to show that the prevalence of water-transmitted diseases could have been much restricted by the use of pure water. Whatever the source of the supply may be, care must be taken to prevent the contamination of the water. When pollution occurs, the use of the water must be discontinued till proper measures have been taken to purify it. The close watching of the water supplies is as important to the dweller in the country as it is to the city inhabitant. It is one of the most important factors in the conservation of the health of the people.

150. Purification of Water. — Boiling is the best household method for killing disease-producing bacteria. In typhoid epidemics, the first regulation should be to boil all water used for drinking or in the preparation of food. The use of boiled water for babies is a familiar application of boiling as a means of purification. There are a number of processes for the purification of water on a large scale, and in most cases they are modifications of the method nature employs. The processes may be roughly classified as mechanical, chemical, and biological. They may be employed separately or together.

---

[1] From Whipple's Value of Pure Water, John Wiley & Sons.

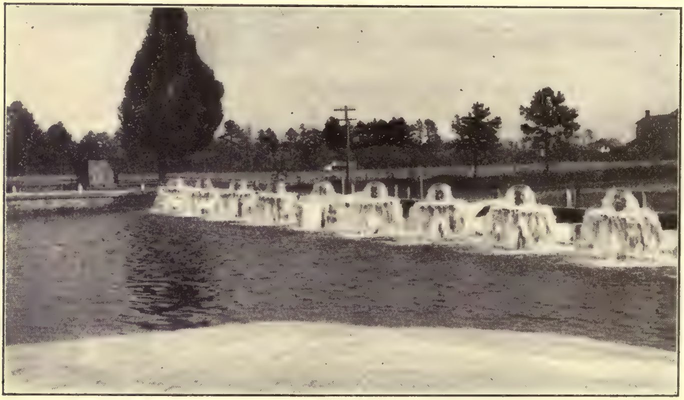


FIG. 66. — AËRATION OF WATER.

151. Aëration. – Aëration means the bringing of water in contact with air, so as to increase the per cent of dissolved oxygen. This is usually done by spouting the water into the air (Fig. 66), or by allowing it to flow down over a steep and rocky slope. A certain amount of purification is accomplished by aëration, but alone it is not to be relied upon. Aëration, however, is very valuable in improving the taste, smell, and appearance of water. The process often gets rid of unpleasant dissolved gases, such as hydrogen sulphide. Other impurities are acted upon by the dissolved oxygen. In running streams the percentage of dissolved oxygen should not fall below 50 % of the amount required for saturation, or else the waters will be unable to rid themselves of organic impurities.

152. Light. — Sunlight is an effective destroyer of germs, but its value is limited in that it reaches only the surface layers of water. The deeper waters of a reservoir may be unaffected. Light brings about the growth of taste-producing algæ, as was the case when the underground waters taken for the Brooklyn supply were exposed in the Ridgewood reservoir.

It is better to store ground and deep-seated waters in the dark; surface waters may be stored either in open or covered reservoirs. It is well to remember that water is uninjured by storage in the dark.

153. Cold. — It has been found that the critical temperature for bacteria is about 0° C. Germs that can pass below that temperature alive have been found to stand even such temperatures as those produced by liquid air. The length of exposure to a freezing temperature, rather than the degree of coldness, is the controlling factor in the vitality of bacteria. Less than 5 % of the bacteria remain alive in ice formed on the surface of deep water. If such ice is stored until the summer months, it is still safer for use. It is never safe, however, to rely upon cold alone for the purification of water. Ice taken from polluted water is unsafe to use.

154. Intermittent Soil Filtration. — Many well waters may be safe to use, although they derive part of their supply from waters which have been polluted. Such waters are filtered as they pass through the soil, and the organic material in them is subjected to the action of nitrifying bacteria. This formation of soluble nitrates from sewage and other waste matter not only requires a supply of oxygen from the air, but *sufficient time* must be allowed for the process. Thus the capacity of the soil for ridding polluted water of its impurities is limited. A steady flow of polluted waters cannot be taken care of. The greatest danger arises in times of heavy rains. Highly protective as soil filtration often is, it is hazardous to depend upon it for pure water from a polluted source.

155. Mechanical Processes of Purification. — The mechanical processes aim to remove from the water the suspended matter, including some of the bacteria. Of these processes, sedimentation and filtration are the chief ones. They are doubly interesting as adaptations of nature's processes of purifying water.

In running water, the coarser sediment usually settles quickly, but the finer particles of clay and suspended organic matter require sufficient time for settling. For this reason sedimentation is carried on either in small settling basins or in storage reservoirs. The water is allowed to remain quiet until the suspended matter goes to the bottom. In the settling basin the treatment requires from a few hours to three days, depending upon the nature and amount of the sediment. When the water is collected in large reservoirs, it stands for a much longer time, and so a much clearer water is obtained.

Experiments have shown that this process of *plain sedimentation* removes a large proportion of the bacteria, but that it is essentially a preliminary process which cannot be relied upon to remove all the dangerous bacteria, particularly in water polluted with sewage.

In many plants for water purification, sedimentation is followed by filtration through mechanical filters or through sand filters. A *mechanical filter* (Fig. 67) is a device for passing water through a layer of sand at a rapid rate. When the sand becomes dirty, it is washed by reversing the current of water. Mechanical filters are used in connection with coagulation, and owe their effectiveness to their straining action rather than to sedimentation in their pores. As the water runs through at a rapid rate, the particles in the water must be large enough to be screened out by the sand and not so numerous as to clog the filter.

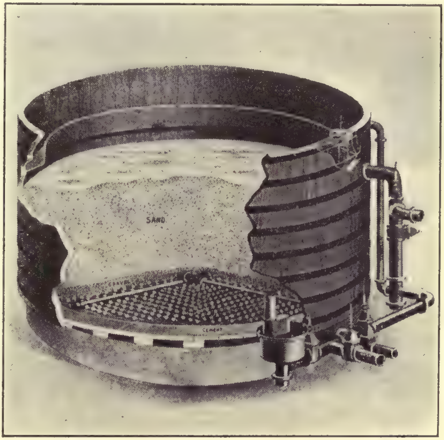


FIG. 67. — MECHANICAL FILTER.

Sand filters (Figs. 68 and 69) have the water run through them at a slower rate than mechanical filters. Their effectiveness is largely due to a gelatinous layer formed on the surface of sand by the organisms in the water. Moreover, in the sand filters, as the upper layer of sand soon becomes dirty and clogged, it is periodically scraped off and washed. In Fig. 70 is shown a line of sand bins with a sand washer in the foreground.

Sand filters are superior to mechanical filters in simplicity of construction, in providing a far greater filtration area for the same cost, and in giving at the slower rate a more thorough straining and bacteriological purification. In many cases, sand filters are used for waters for which a rough, inexpensive process suffices, because

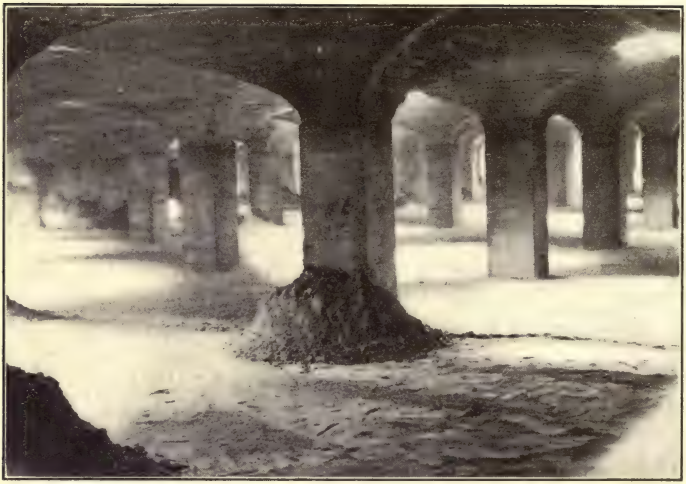


FIG. 68. — SAND FILTERS.

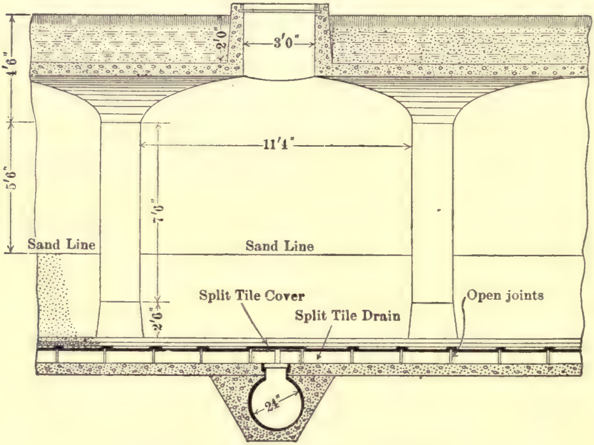

4'6"
5'6"
2'0"
3'0"
11'4"
7'6"
2'6"
Sand Line
Sand Line
Split Tile Cover
Split Tile Drain
Open joints
24"

FIG. 69. — SAND FILTERS. (SECTIONAL.)

they are not turbid enough to require a preliminary treatment.

156. Sedimentation with Coagulation. — The process of *plain sedimentation* described in § 155 is not effective when the suspended matter is in a finely divided state. In such cases, sedimentation is aided by the use of a gelatinous substance produced by a chemical reaction. The whole process is known as a sedimentation with coagulation. The coagulant employed is usually aluminum hydroxide.

FIG. 70. — EXTERIOR OF WATER FILTRATION PLANT.

When limewater is added to a solution of aluminum sulphate, a white gelatinous precipitate of aluminum hydroxide is formed:

$$\underset{\text{aluminum sulphate}}{Al_2(SO_4)_3} + \underset{\text{calcium hydroxide}}{3\,Ca(OH)_2} \longrightarrow \underset{\text{aluminum hydroxide}}{2\,Al(OH)_3} + \underset{\text{calcium sulphate}}{3\,CaSO_4}$$

When this reaction occurs in water containing suspended matter, the particles in suspension become entangled in the gelatinous hydroxide. This coagulant carries down with it the greater part of the sediment and the disease germs in the water. When the coagulant with its entrapped impurities is removed by some mechanical device, the water is left comparatively pure.

Many natural waters are temporary hard waters, in that they contain in solution either calcium, magnesium, or ferrous bicarbonates, or mixtures of these. These bicarbonates themselves react with aluminum sulphate to form aluminum hydroxide without the use of lime:

$$\underset{\substack{\text{aluminum}\\ \text{sulphate}}}{Al_2(SO_4)_3} + 3\,\underset{\substack{\text{calcium}\\ \text{bicarbonate}}}{CaH_2(CO_3)_2} \longrightarrow \underset{\substack{\text{aluminum}\\ \text{hydroxide}}}{2\,Al(OH)_3} + 3\,\underset{\substack{\text{calcium}\\ \text{sulphate}}}{CaSO_4} + 6\,\underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2}$$

In water purification plants, the temporary hardness of the water is determined, and then a calculated amount of aluminum sulphate is added so as to react with all the bicarbonate. In waters requiring both the aluminum sulphate and the calcium hydroxide, such amounts of lime (CaO) and aluminum sulphate are used as will not leave an excess of either after the reaction has taken place. The amounts of chemicals required per million gallons of water are usually astonishingly small. Even the calcium sulphate formed by the reaction, which remains for the most part in the water, does not render it excessively hard or unfit for drinking.

157. Other Chemical Processes of Purification. — Chlorine and ozone are two substances that have recently come into use as effective in purifying water. In the *chlorination processes* chlorine is produced from some hypochlorite, as sodium hypochlorite or calcium hypochlorite (bleaching powder). The nascent chlorine generated is most vigorous in its germicidal action. Jersey City, New Jersey, has a successful plant of this type.

In the *ozone processes*, the ozone is produced by electric discharges in special apparatus known as ozonizers, and then is allowed to bubble up through long cylinders to which water is admitted at the top. These streams of extremely minute bubbles of ozone destroy all forms of bacterial life. Ozone is preferable to chlorine, as an excess of ozone in the water is not objectionable, while even a slight excess of unused chlorine is highly undesirable. In St. Petersburg, the much-polluted waters of the Neva are rendered safe for drinking by the ozone process. Paris has recently installed an ozone plant which purifies most successfully the dirty water of the Seine. Turbid waters always undergo a preliminary treatment before being chlorinated or ozonized.

158. Hard Waters. — In the narrow sense, hard waters are those which contain in solution salts of calcium and magnesium, particularly their carbonates and sulphates. The term, however, has been extended to include waters containing iron compounds and certain other soluble salts. A better definition of hard water would be to describe it as *water containing mineral substances that precipitate or curdle soap.* Water containing sodium chloride resembles hard water in this action, because the salt decreases the solubility of the soap.

Water that contains less than 25 parts of such dissolved substances per million parts of water is not noticeably hard. When the hardness is above 50 parts per million, the water is classed as distinctly hard; above 100 parts it will be known as very hard. In some cases a hardness of 200 or 300 parts per million exists.

Hard waters are of two kinds — permanent and temporary. Waters that are not softened by boiling in an open vessel are permanent hard waters; temporary hard waters are softened by such boiling.

159. Temporary Hard Waters. — These contain in solution either the bicarbonate of calcium, of magnesium, of ferrous iron, or mixtures of these. The production of such a hard water is typified by the natural formation of calcium bicarbonate. When the surface waters drain through the soil, they absorb carbon dioxide formed by the decaying of organic matter. Carbonic acid is formed in the water:

$$\underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2} \longrightarrow \underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_3}$$

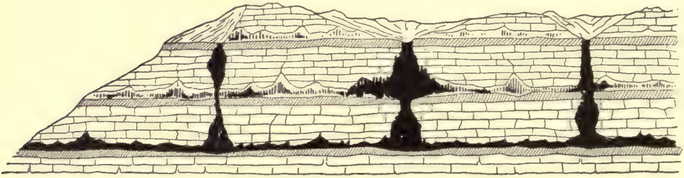


FIG. 71. — SECTION OF CAVES IN LIMESTONE REGION.

When the water containing carbonic acid flows over limestone, the calcium carbonate, of which it is mainly composed, dissolves (Fig. 71), forming calcium bicarbonate, a soluble substance:

$$\underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_3} \longrightarrow \underset{\substack{\text{calcium}\\\text{bicarbonate}}}{CaH_2(CO_3)_2}$$

When this temporary hard water is boiled, the following decomposition occurs:

$$\underset{\substack{\text{calcium}\\\text{bicarbonate}}}{CaH_2(CO_3)_2} \longrightarrow \underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

The calcium carbonate precipitates and the carbon dioxide escapes as a gas.

Temporary hard water containing ferrous bicarbonate, $FeH_2(CO_3)_2$, is similarly decomposed by boiling, but the decomposition is complicated if the oxygen of the air gains access to the precipitate. The total action may be represented by the equation:

$$\underset{\substack{\text{ferrous}\\\text{bicarbonate}}}{4\,FeH_2(CO_3)_2} + \underset{\text{water}}{2\,H_2O} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{ferric}\\\text{hydroxide}}}{4\,Fe(OH)_3} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{8\,CO_2}$$

Ferric hydroxide, on further drying, is converted into a compound resembling iron rust. An iron hard water undergoes the changes just mentioned simply on standing in contact with air.

160. Permanent Hard Waters. — Gypsum, $CaSO_4.2\,H_2O$, is one of the most widely and abundantly distributed minerals. On this account, and because of its solubility in water, most permanent hard waters contain calcium sulphate, $CaSO_4$. Magnesium sulphate, $MgSO_4$, is also frequently found in permanent hard waters.

161. Hard Waters and Soap. — Soft water, or water free from dissolved mineral salts, readily forms lather with soap. When, however, soap is used with a hard water, part of the soap is wasted by combining chemically with the dissolved substances in the water to form an insoluble soap. The reaction in the case of calcium sulphate may be illustrated by the equation:

$$\underset{\substack{\text{sodium}\\\text{stearate (soap)}}}{2\,NaC_{18}H_{35}O_2} + \underset{\substack{\text{calcium}\\\text{sulphate}}}{CaSO_4} \longrightarrow \underset{\substack{\text{calcium}\\\text{stearate}}}{Ca(C_{18}H_{35}O_2)_2} + \underset{\substack{\text{sodium}\\\text{sulphate}}}{Na_2SO_4}$$

The calcium stearate is a white curd-like precipitate. Until all the calcium is precipitated out of the hard water, the water will not form suds freely.

The soap-destroying qualities of hard water is a decided factor in the cost of soap for household use. It has been found that one pound of average soap will soften about 200 gallons of water that has a hardness of 25 parts per million. An increase of 1 part per million in hardness means an increase of $10 in the cost of soap to soften a million gallons of water.

Although the waste of soap is the principal disadvantage of hard waters for household use, it is not the only one. The precipitates of calcium and magnesium stearates fill the pores of the skin, making thorough cleansing difficult. In the laundry these precipitates get between the fibers of the clothes, giving a dingy appearance after washing. Hard waters tend to encourage the use of soaps or washing powders that contain considerable free alkali. Such cleansing agents are injurious to fabrics. The unsightly scums in wash basins and bath tubs are mainly due to deposited calcium and magnesium soaps.

162. Boiler Scale. — When hard waters are heated, a deposit or scale is formed on the inside of the boiler, kettle, or pipe (Fig. 72). In time this becomes of sufficient thickness to retard greatly heating the water. It has been estimated that a layer of calcium sulphate scale offers from twenty to fifty times as much resistance to the conduction of heat as an equal thickness of wrought iron. The formation of such scale depends upon change in solubility due to an increase in temperature or to certain chemical reactions.

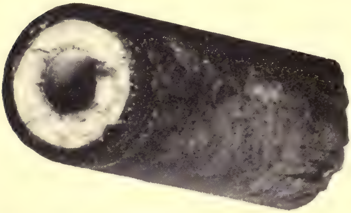


Fig. 72. — Pipe from Water Back in Stove showing Scale.

When a temporary hard water is heated, the bicarbonates are decomposed:

$$\underset{\substack{\text{calcium}\\\text{bicarbonate}}}{CaH_2(CO_3)_2} \longrightarrow \underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

The calcium carbonate is deposited as a soft, powdery scale which may be removed by "blowing off" the boiler. Magnesium carbonate is similarly deposited from the soluble magnesium bicarbonate. On further heating in the boiler, the magnesium carbonate is changed into magnesium hydroxide which settles out:

$$\underset{\substack{\text{magnesium}\\\text{carbonate}}}{MgCO_3} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\substack{\text{magnesium}\\\text{hydroxide}}}{Mg(OH)_2} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

The calcium sulphate in permanent hard waters becomes almost insoluble when the water under pressure in the steam boiler reaches a temperature of 120° C. (250° F.). This sulphate forms a hard, crystalline scale, which is so adherent that it sometimes has to be chiseled off from the inside of the boiler. Calcium sulphate while depositing often acts as a binding material on the calcium and magnesium carbonates, magnesium hydroxide, clay, and sand precipitated or suspended in boiler waters. In this manner scales are formed which are difficult to remove.

Another source of boiler scale is lubricating oil which gets into the boiler water. The floating particles become coated with a scum, and, sinking to the bottom, form an incrustation which is an exceedingly poor conductor of heat.

163. Disadvantages of Boiler Scale. — The increase in the total cost of coal due to boiler scale is a serious item to steam producers. A scale $\frac{1}{8}$ inch in thickness means a decided loss in the heating efficiency of the fuel. Moreover, the boiler shell may become overheated and burnt (oxidized). The different rates of expansion of boiler scale and iron lead to strains which cause leaks.

164. Corrosion or Pitting. — Hard waters lessen the life of a boiler and its tubes by corrosion or pitting. This may be due in part to carbon dioxide and oxygen dissolved in the water. Salt water is too corrosive to be used in boilers. Swampy waters may be very corrosive from the presence of carbonic, tannic, humic, and other acids. Water from mining districts often contains mineral acids, particularly sulphuric acid, from the oxidation of ores containing sulphur.

165. Foaming. — Another serious disadvantage of hard waters is the foaming they may cause in steam boilers. Foaming is a violent frothy ebullition of the water in the boiler, and is caused by an excess of impurities. The scale-forming material precipitates as a fine powder, each particle of which acts as a point of steam formation. The excess of alkaline salts in some waters makes the water foam as soon as it is heated in the boiler. The best way to prevent foaming is to use clean water in a clean boiler.

166. Hard Waters in Chemical Industries. — Hard waters are unsuitable for use in dye works. The dyes do not dissolve well, the colors are frequently altered, and the goods may be unevenly dyed, even to the extent of spotting. In the tanning of leather, a hard water may prevent the proper absorption of tannin, resulting in brown stains on the leather. In sugar refining, the compounds that give water its hardness may be absorbed by the animal charcoal, thus lessening the power of this substance to decolorize or bleach the sirup filtered through it.

Waters containing iron compounds are objectionable in the manufacture of pulp and paper, as brown stains are formed. Even an ordinary hard water may interfere with the sizing of the paper. Only within a few years have chemical manufacturers come to a realization of the value of pure water in their operations.

167. Water-Softening. — The recognized disadvantages of hard waters in steam production and in the chemical industries have led to the establishment of water-softening plants. The operation of these depend upon a few chemical reactions in which lime and sodium carbonate are the important chemicals.

When limewater is added to a calcium temporary hard water, the following reaction occurs :

$$\begin{array}{ccccccc} CaH_2(CO_3)_2 & + & Ca(OH)_2 & \longrightarrow & 2\,CaCO_3 & + & 2\,H_2O \\ \text{calcium} & & \text{calcium} & & \text{calcium} & & \text{water} \\ \text{bicarbonate} & & \text{hydroxide} & & \text{carbonate} & & \end{array}$$

Magnesium bicarbonate is similarly decomposed by calcium hydroxide :

$$\begin{array}{ccccccccc} MgH_2(CO_3)_2 & + & Ca(OH)_2 & \longrightarrow & MgCO_3 & + & CaCO_3 & + & 2\,H_2O \\ \text{magnesium} & & \text{calcium} & & \text{magnesium} & & \text{calcium} & & \text{water.} \\ \text{bicarbonate} & & \text{hydroxide} & & \text{carbonate} & & \text{carbonate} & & \end{array}$$

Since magnesium carbonate is more soluble than calcium carbonate, an additional quantity of lime must be used so as to form insoluble magnesium hydroxide :

$$\begin{array}{ccccccc} MgCO_3 & + & Ca(OH)_2 & \longrightarrow & Mg(OH)_2 & + & CaCO_3 \\ \text{magnesium} & & \text{calcium} & & \text{magnesium} & & \text{calcium} \\ \text{carbonate} & & \text{hydroxide} & & \text{hydroxide} & & \text{carbonate} \end{array}$$

Permanent hard waters are softened by the use of sodium carbonate in its cheaper form of soda ash :

$$\underset{\substack{\text{calcium}\\ \text{sulphate}}}{CaSO_4} + \underset{\substack{\text{sodium}\\ \text{carbonate}}}{Na_2CO_3} \longrightarrow \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\substack{\text{sodium}\\ \text{sulphate}}}{Na_2SO_4}$$

In case the permanent hard water contains magnesium sulphate, lime is used in addition to the soda:

$$\underset{\substack{\text{magnesium}\\ \text{sulphate}}}{MgSO_4} + \underset{\substack{\text{sodium}\\ \text{carbonate}}}{Na_2CO_3} + \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{Ca(OH)_2} \longrightarrow$$

$$\underset{\substack{\text{magnesium}\\ \text{hydroxide}}}{Mg(OH)_2} + \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\substack{\text{sodium}\\ \text{sulphate}}}{Na_2SO_4}$$

The sodium sulphate formed in the reaction above is very soluble and not particularly harmful.

Water for boilers is best softened before it is fed into the boiler. In stationary boiler plants this is often partly accomplished in the feed-water heater, which utilizes the heat of the waste steam or of the fuel gases. The steam enters at the bottom of the heater and comes in contact with water sprayed in or splashed against plates. The water is then filtered through burlap or some similar material on its way to the boiler.

168. Water-Softeners. — The demand for water-softeners has led to the manufacture of numberless *boiler compounds* in which cheap chemicals, such as lime, sodium carbonate (soda ash), sodium fluoride, sodium aluminate, and sodium phosphate, have been put up and sold for fancy prices to engineers. Glutinous, starchy, and oily substances are also sold for water softeners. They are supposed to surround the scale-forming particles mechanically and prevent their cementing into a scale. These substances are not particularly effective, as they thicken and foul the water more than they prevent the formation of a hard scale. Kerosene is the best representative of a class of water-softeners that act mechanically and also loosen the deposited scale. Boiler graphites are also widely used.

A water-softener for boilers should precipitate the salts in a powdered condition so that they may easily be blown off. Moreover the softener should contain neither acids nor compounds yielding acids. Engineers in most cases can rely on lime and soda as cheap and effective remedies for hard water.

169. Softening Plants. — Industrial establishments requiring large quantities of softened water usually find it economical to install water-softening plants. In these the initial precipitations are carried on in tanks or settling basins, with carefully calculated amounts of chemicals based on the analysis of the water. After the settling, the complete removal of the precipitate is accomplished by some form of rapid filter, as cloth filter presses, sand filters, or specially devised filters of metal.

SUMMARY

Natural Waters contain gases from the air, inorganic and organic substances from the soil, and lower forms of plant and animal life.

The Value of a Drinking Water depends upon its color, taste, odor, turbidity, and the absence of impurities harmful to the body.

Diseases may be transmitted by water.

Sterilization of Water by boiling is a good household method. Natural processes of purification are by aëration, light, cold, and intermittent soil filtration.

Artificial Methods of Water Purification are generally adaptations of the natural processes. Among the chemical means employed are sedimentation with a coagulant like aluminum hydroxide, chlorination, and the use of ozone.

Hard Water is water containing mineral substances that precipitate or curdle soap. They waste soap, interfere with laundering, form scale in boilers, and lessen the efficiency of many industrial operations.

Temporary Hard Waters contain in solution the bicarbonate of calcium, of magnesium, of ferrous iron, or mixtures of these. They may be softened by boiling or by the addition of an alkali.

Permanent Hard Waters usually owe their hardness to calcium sulphate, but magnesium sulphate and other dissolved salts are sometimes found. They may be softened with sodium carbonate.

EXERCISES

1. What are the advantages of pure water?

2. Distinguish between surface and ground waters.

3. How does each of the following get into natural waters: oxygen, carbon dioxide, ammonia, nitrates and nitrites, common salt, sulphates, and bacteria?

4. State the desirable characteristics of wholesome drinking water.

5. To what do natural waters owe their color? Their turbidity?

6. Account for the disagreeable odors and tastes of some waters.

7. Why does freshly distilled water taste "flat"?

8. What diseases may be transmitted by water? What epidemics in your state have been ascribed to impure water?

9. When and why should water for drinking and cooking be boiled?

10. How does aëration purify water?

11. What effect does light have on natural waters?

12. Is it ever safe to use ice taken from a contaminated pond or river? Explain.

13. What are the limitations to the purification of water by intermittent soil filtration?

14. How does *plain sedimentation* purify water?

15. Explain the use of a sand filter.

16. Explain, with the aid of an equation, the use of aluminum hydroxide as a coagulant.

17. Compare the chlorine and the ozone processes of purification.

18. Define: (*a*) hard water; (*b*) temporary hard water; (*c*) permanent hard water.

19. How is soap wasted by hard waters? Equation? What other disadvantages have hard waters for household use?

20. Write an equation to show the softening of a temporary hard water by (*a*) boiling, (*b*) the addition of lime.

21. How would you soften a permanent hard water containing calcium sulphate?

22. What is boiler scale? Briefly state how it is formed. How does it waste coal?

23. What are "boiler compounds"? What is their value?

CHAPTER XVIII

TYPICAL PROPERTIES OF METALS

In addition to the similarities in the chemical behavior of metals which have been noted in the chapters on Acids, Bases, and Salts, there are certain physical characteristics typical of metals. The extent to which each metal possesses these various properties determines its usefulness.

170. Conductivity. — All metals conduct both heat and electricity. When a silver spoon is put into a cup of coffee, the heat of the liquid is conducted to the end of the spoon. When the poles of an electric battery or of a dynamo are joined with a copper wire, an electric current flows through the wire. The best conductor of both heat and electricity is silver, while copper is nearly as good. Gold and aluminum rank next for both kinds of conduction. The other metals rank in about the same order for heat and electrical conductivity, though the same metal may differ in the percentage of its heat and electrical conductivity as compared to copper. Thus, the electrical conductivity of iron is about $\frac{1}{6}$ that of copper, while its heat conductivity is about $\frac{1}{8}$. In general, metals rank higher than other substances in conductivity of both kinds.

171. Malleability. — It is characteristic of metals that they may be rolled or hammered into thin sheets. This property is malleability. Gold is the most malleable substance known; that is, it may be beaten into the thinnest sheets.

Gold leaf $\frac{1}{300,000}$ of an inch thick has been made. Silver and copper can be rolled and hammered into thin sheets and foil. Sheet lead was formerly extensively used as roofing and is now used for lining acid tanks. Lead foil is used to line chests of tea, and is often substituted for tin foil. Wrought iron can be worked into a great variety of forms by hammering when hot (Fig. 73). Sheet iron is made from ingots of wrought iron by rolling between hardened steel rolls. Hammering or rolling tends to harden metals and make them more brittle, and so they are generally "annealed" or softened by heating to redness and then cooling slowly several times during the sheet-making process. Zinc has the peculiar property of being brittle at ordinary temperatures, but is malleable between 100° C. and 140° C. Sheet zinc rolled between these temperatures retains its malleability when cooled to ordinary temperatures.

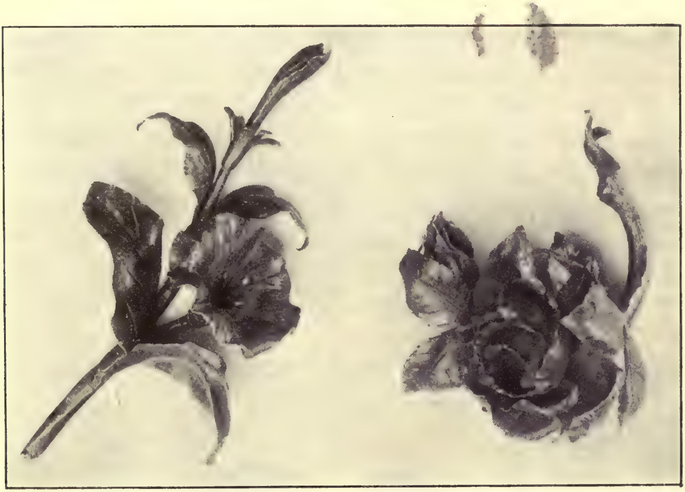


FIG. 73. — MALLEABILITY OF IRON.

172. Ductility. — Some metals are ductile, that is, they can be drawn into wire. In making wire, the metal is first rolled into a rod about 0.2 of an inch thick. This rod is thoroughly soaked in dilute acid to remove scale, coated with lime, and the end pointed. The pointed end is drawn through a conical hole (Fig. 74) in a steel drawplate, the hole having a diameter slightly less than the rod. By repeating the process with smaller and smaller holes, wire of the desired size may be finally produced (Fig. 75). During the process the wire is kept lubricated, part of the time with flour and part of the time with a mixture of grease and sulphuric acid, called "soap." As in the case of rolling, wire drawing hardens the metal and it must be frequently annealed.

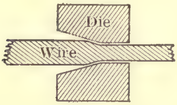


FIG. 74.

The fineness of the smallest size wire that can be drawn from a metal is a measure of its ductility. Platinum, gold, silver, and iron are among the most ductile metals. Plati-

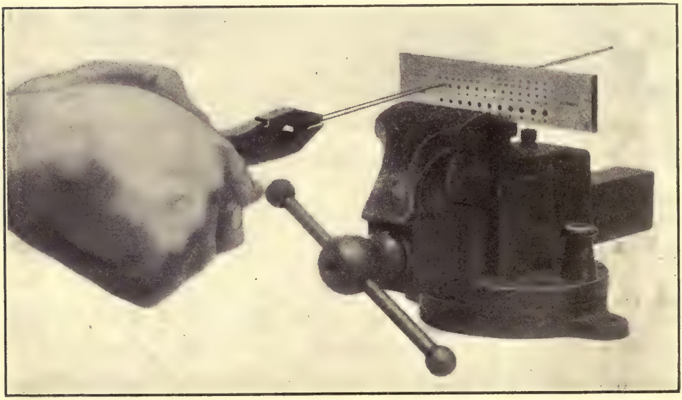


FIG. 75. — LABORATORY WIRE DRAWING.

num can be drawn by a special process into wires less than 0.001 of an inch in diameter. To be highly ductile, a metal must be very tenacious. Steel wire is made that will endure, before it breaks, a pull of more than 120 tons for a square inch of cross section of wire. The tensile strength of wire per square inch is higher than that of the rods from which it was drawn. Wrought-iron wire has about a third of the tensile strength of the best steel wire, but is much more flexible and is cheaper and for these reasons is much used. Copper has much less tensile strength, but is very ductile and its electrical conductivity is very important. Recently aluminum wire has replaced copper to a considerable extent for transmission lines, as an aluminum wire is lighter and has greater tensile strength than a copper wire which will carry the same electrical current. Lead, tin, and zinc cannot be drawn into fine wire. Lead fuse wire is made by squeezing lead through a die by means of a hydrostatic press. Malleability and ductility are often characteristic of the same metal, but lead and tin are highly malleable, without being ductile.

173. Fusibility. — With the exception of mercury, which is a liquid at all temperatures above – 39° C., the common metals have high melting points. The more refractory, such as platinum and tungsten, require a temperature of more than 1700° C. to melt them. Such metals are commonly melted in the electric arc furnace. Of the common metals, iron has the highest melting point, and tin the lowest. Sodium and potassium generate enough heat in their reaction with water, to keep them in molten drops on the surface of the water (§ 22).

The wide range of melting points in the alloys will be shown in the discussion of that subject. The following table shows the more important metals arranged according to their melting points:

METAL	MPT. ° C.	METAL	MPT. ° C.	METAL	MPT. ° C.
Mercury	– 39	Zinc	419	Iron (pig)	1075
Tin	232	Aluminum	657	Iron (pure)	1505
Bismuth	270	Silver	955	Platinum	1753
Cadmium	322	Gold	1062	Tungsten	2800
Lead	327	Copper	1065	Tantalum	2900

174. Hardness. — Hardness may in general be defined as resistance to change of shape before breaking. Two substances are usually compared as to hardness by finding which will scratch or cut the other. A diamond scratches glass; a steel knife blade scratches lead. We say that the diamond is harder than glass, the steel harder than the lead. Tool steel is harder than machine steel. But a hardened steel tool which will cut machine steel easily will scarcely scratch some cast-iron. Tempering, the sudden cooling of a metal from a red or a white heat, often increases the hardness, notably in the case of steel. The outer layer of cast-iron is much harder than the interior.

All the common metals are hard, as compared to wood. Among the hardest metals are tempered steel, nickel, and iron. Brass, an alloy of copper and zinc, is harder than copper, but softer than iron. Zinc is softer than copper, and lead can readily be cut with a knife. Some of the less familiar metals, such as sodium and potassium, can be cut almost as readily as cheese. No comparative table of hardness is given here, as the metals rank differently according to the form in which they are prepared and also according to the kind of test for hardness that is made.

ALLOYS

175. Physical Constitution of Alloys. — Alloys are usually made by melting together two or more metals to form a metallic substance of practically uniform composition, having definite properties of its own. In the case of amalgams, which are alloys of mercury, melting is not always necessary, as the other metal or metals dissolve in the mercury. It is very convenient to think of the alloys as solutions of one solid metal in another solid metal, and so the term *solid solutions* is often applied to them. In most alloys, the metals do not appear to form compounds, although there are a few cases in which an alloy may consist of a compound of two metals dissolved in an excess of one of them. Like solutions, alloys have their constituents intimately mixed and quite uniformly distributed throughout the mass. The microscope, however, usually shows that, except in the case of the metallic compounds mentioned above, the distribution is not uniform, but that the different constituents can often be distinguished in the form of plates or crystals. This is not unlike the result obtained from the freezing of a solution of salt and water, in which the crystals of salt and crystals of ice lie side by side and can be distinguished by magnifying the salt ice obtained.

Some metals alloy in all proportions, just as alcohol and water dissolve each other in all proportions. In other cases, one metal will alloy with another only up to a certain fixed ratio. When one metal dissolves in another, the melting point is usually lowered just as the freezing point of a solution is lower than that of the solvent. There is one particular alloy of two metals that is more fusible than any other alloy of the same two metals, but the proportions in this more fusible alloy are not those of their atomic weights. So in the great majority of cases, at least, the alloys are mixtures or solid solutions, and not chemical compounds.

176. Fusible Metals. — An alloy often shows physical properties which are intermediate between those of the metals composing it. Sometimes, however, its hardness, or fusibility, or ductility may greatly exceed the corresponding property of any of the metals contained in the alloy. Sodium and potassium, with individual melting points of 97° and 62°, respectively, form an alloy which is liquid at ordinary temperatures. *Solder* is an alloy of lead and tin in various proportions, according to the melting point desired; "half and half," which consists of equal parts of the two metals, has a melting point of 188° C., which is less than that of either metal. Harder or less fusible solders have a larger proportion of lead, and soft or easy solder has a large proportion of tin. A very fusible solder can be made from equal parts of lead, tin, and bismuth; this melts at 121° C.

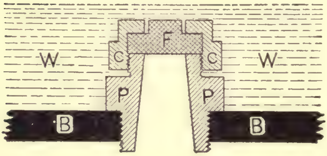


FIG. 76. — SAFETY PLUG.

Fusible alloys, consisting wholly or largely of lead, tin, and bismuth, are used in the plugs of automatic sprinkler systems, and in safety plugs for steam boilers (Fig. 76). Most of the steam boiler plugs contain zinc instead of tin. As long as the plug (F) is covered with water, its temperature remains that of the surrounding water (W). When it becomes uncovered, it reaches the temperature of the heated shell of the boiler (B) and so melts, allowing steam to escape and giving warning of low water. Wood's alloy, often used in sprinkler systems, contains lead, tin, bismuth, and cadmium and melts at 60° C. (140° F.). A fire in a room provided with sprinklers plugged with this or a similar alloy, would soon melt the plugs, permitting the water to gush out and extinguish the fire.

177. Bearing Metals. — It is highly desirable that the bearings in which the axles of machinery run should be lined with a metal which shall be softer than the axle, and so wear away faster. It should also be fusible, so as to melt and run out if the bearing becomes overheated. Babbitt metal is the best known of these bearing alloys. Tin, lead, and antimony, or tin and zinc are the chief constituents of commercial Babbitt. The original Babbitt consisted of 3–7 parts copper, 88–89 parts tin, and 7–4 parts antimony. The metal in brass bearings is from 65 % to 92 % copper, the remainder being usually tin and lead. All of these bearing metals produce less friction with a steel shaft than would be caused by a steel or iron bearing.

178. Amalgams. — These have already been defined as alloys of mercury with other metals. They are soft when first formed, but soon harden into a crystalline mass. The silver amalgam used by dentists for filling teeth is typical. The powdered silver and other metals are mixed with the mercury and the excess of the latter squeezed out. When forced firmly into the cavity, the amalgam takes a hard, crystalline form in a few hours. Zinc used in voltaic cells is usually amalgamated by cleaning with acid and then rubbing mercury on the surface of the zinc. In this way a surface of pure zinc is constantly presented to the acid for action, and the zinc lasts longer.

The tendency of gold and silver to amalgamate with mercury is utilized in separating these metals from the quartz, or other rock material, which is found associated with them in the earth. The finely ground mixture of metal and rock is carried by a thin stream of water over the surface of tables coated with mercury. The precious metal amalgamates with the mercury and the rock material is carried off by the water. The mercury is separated by distillation from the amalgam, leaving the precious metal ready for refining. An amalgam of tin and mercury was formerly used on the back of mirrors, but its place has been taken by a film of pure silver, formed by the reduction of silver nitrate with which the glass has been coated.

179. Brass and Bronze. — The essential constituents of brass are copper and zinc, in varying proportions, according to the use to which it is to be put. There is usually about twice as much copper as zinc, and small percentages of lead and tin are often present. When a red brass is desired, as for buttons to be gold plated, the percentage of copper may run as high as 80 % or even 90 %. Brass used for electrical purposes has a high percentage of copper, to increase its conductivity. Brass is highly malleable and ductile.

The name *bronze* is applied to a great number of alloys, which are essentially copper and tin, although a small percentage of zinc and sometimes of other metals is often present. The percentage of copper in bronze is higher than is that in ordinary brass, being from 80 % to 90 %. Bronze for statuary contains both lead and zinc, with a reduction in the proportion of tin. *Bell metal* is a bronze with a large proportion of tin. *Phosphor bronze* contains from 0.2 % to 4 % of phosphorus in the form of phosphide of copper or phosphide of tin. It is very hard and tenacious and is not corroded by water. These properties make it valuable for water wheels and propellers, as well as for other uses demanding a metal not readily altered by wear or moisture.

180. German Silver. — This alloy is a white metal containing from 18 % to 30 % nickel alloyed with copper and zinc, 3 or 4 parts of copper being used to 1 of zinc. It is hard, takes a high polish, and is not easily corroded. The electrical resistance of German silver is from 18 to 28 times as great as that of copper, and it is largely employed as resistance wire in electrical work. It is also used for making small articles and is the "white metal" used for the interior of plated ware.

181. Type Metal. — Lead and antimony are here the important metals and from 10 % to 20 % of tin is added to increase the fusibility. The antimony gives hardness to the softer lead and tin. It also causes the alloy to expand when it solidifies, thus filling all the outlines of the mold or matrix, and so making a clean-cut impression. Books are not printed from type, as type metal is not hard enough to stand the wear involved in printing large editions without becoming dull, so copper-faced electrotype plates made from the type are used instead (see § 415). These plates can be preserved for future editions, and the type used again to prepare other plates.

182. Light Alloys. — For many purposes, such as automobile and aëroplane parts, lightness combined with tensile strength is the most important feature of an alloy. For such alloys aluminum is used as a base, and the tensile strength and uniformity of the castings is increased by the addition of other metals. *Aluminum bronzes* consist of aluminum alloyed with copper and zinc, or copper and nickel. They combine lightness, hardness, and a tensile strength from once to twice that of cast iron. *Magnalium* and other aluminum-magnesium alloys contain from 2 % to 10 % of magnesium, alloyed with aluminum. This does not increase the weight of the alloy, but gives it a tensile strength nearly that of machine steel. The future use of aluminum for machine parts will depend upon the perfecting of its alloys.

183. Coins. — Our gold and silver coins contain 10 % copper, which increases their hardness and so causes them to wear longer. English gold pieces contain 8.33 % copper, and English silver money, 7.5 % copper. Sterling silver has the same composition as English silver coins. Our nickel five-cent pieces are 75 % copper and 25 % nickel, while pennies contain 3 % of tin and 2 % of zinc with 95 % copper.

The proportion of alloy metal used with gold for purposes other than coinage is not usually given in per cent, but in "carats." Pure gold is 24 carats fine; 18-carat gold is $\frac{18}{24}$ gold and $\frac{6}{24}$ copper or silver. This carat is not to be confused with the carat used as a weight for precious stones, which is equal to 200 milligrams.

SUMMARY

Metals are **good conductors** of both heat and electricity. Silver, copper, gold, and aluminum are the best conductors.

Most metals can be rolled or hammered into thin sheets. Gold, silver, tin, aluminum, and copper are very **malleable.**

Some metals can be drawn into wire by passing them through a tapering hole in a steel plate. Platinum, gold, silver, copper, and iron are especially **ductile.**

Both rolling and wire drawing harden metals, so they must be **annealed** to keep them from becoming brittle.

The common metals, except mercury, have **high melting points.**

Metals show various degrees of **hardness.** Tempering increases and annealing diminishes hardness.

Alloys are solid solutions of two or more metals. They are not usually chemical compounds. The physical properties of alloys are not always intermediate between the properties of the metals composing them. Many alloys have a lower melting point than any of their constituents, *e.g.* solder and fusible alloys.

IMPORTANT ALLOYS

NAME	CONSTITUENTS
Aluminum bronze	Aluminum, copper and zinc or nickel
Amalgams	Mercury with other metals
Bearing metal	Copper, tin, lead, antimony
Brass	Copper and zinc
Bronze	A brass with tin, and sometimes with other metals
Coins	Gold and copper; silver and copper; copper and nickel; copper, tin, and zinc
Fusible metal	Lead, bismuth, and tin or zinc
German silver	Nickel, copper, and zinc
Magnalium	Aluminum and magnesium
Solder	Lead and tin
Type metal	Lead, antimony, and tin

EXERCISES

1. Why is copper often used for wash boilers?

2. Which is better, an iron teakettle or an aluminum teakettle? Why?

3. Name three metals or alloys used as electric conductors. Which is the best conductor? Why are the other materials used?

4. Name four kinds of foil and give a use of each.

5. Why is lead wire manufactured by a different process from copper wire? Describe the process in each case.

6. Why is it harder to keep the solder fluid when soldering copper than when soldering tinware?

7. Why may an empty tin pan be ruined by placing it on a red-hot stove?

8. Why could not a mercury thermometer be used by Arctic explorers?

9. Arrange five common metals in the order of their hardness. If you were in doubt as to the relative hardness of two metals, how would you determine it experimentally?

10. What is an alloy? A solid solution? Why are the alloys not regarded as chemical compounds?

11. Explain the working of an automatic sprinkler system.

12. Why can a piece of tinware be soldered without melting the tin coating off the iron?

13. In soldering an additional part to an article already soldered, would you use hard or soft solder? Why?

14. What is Babbitt metal? Why are machine bearings always lined with this or some similar material?

15. Explain the production and use of gold, silver, and zinc amalgams.

16. Give the composition and uses of each of the following: brass; bronze; phosphor bronze; aluminum bronze.

17. Give the composition of a ten-dollar gold piece, a quarter, a nickel, a penny.

18. Which is more valuable, a sterling silver spoon or a spoon of the same size made of coin silver?

19. Give the percentage composition of 10-carat, 14-carat, and 18-carat gold rings.

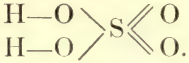
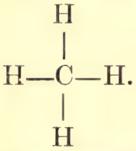
CHAPTER XIX

CARBON COMPOUNDS

HYDROCARBONS, SUBSTITUTION PRODUCTS, AND ALCOHOLS

184. Nature of Organic Compounds. — The beginner in chemistry soon becomes familiar with a few carbon compounds, such as carbon monoxide, carbon dioxide, and the carbonates of sodium, potassium, ammonium, and calcium. These compounds are not very different from the similar compounds of other elements. The majority of elements form comparatively few compounds and these are simple in structure. Carbon, however, forms numerous compounds, complex in structure, and widely varying in properties. In fact, the chemistry of *carbon compounds* is so wide a domain that most students of chemical science merely touch upon its borders. This division of the subject is often termed *Organic Chemistry*, an old name that was given when it was believed that the complex carbon compounds could be produced only in the living tissues of plants and animals. Years of patient investigation, however, have made it possible to produce in the laboratory many of the compounds found in the living world, as well as hundreds of others that have not yet been found in nature.

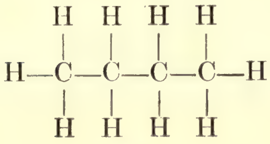
The remarkable power of carbon to form compounds is due to two things — its high valence (combining power) of four, and the ability of the carbon atoms to unite with each other. These facts are well illustrated by the *hydrocarbons*, a class of carbons containing only the two elements hydrogen and carbon. To imagine the arrangement of the atoms in the hydrocarbons, it is convenient to use graphic formulas. In these, each unit of valence is represented by a short straight line.

Thus, hydrogen chloride may be shown H—Cl. The short straight line shows a valence of one for each of the combining elements, hydrogen and chlorine. A graphic formula for water is H—O—H. This shows the valence of the oxygen atom as two. We represent hydrogen peroxide H—O—O—H and sulphuric acid  $\begin{matrix}H{-}O\\H{-}O\end{matrix}\!\!>S\!\!<\!\!\!\begin{matrix}O\\O\end{matrix}$. The simplest hydrocarbon is marsh gas or methane,  $\begin{matrix}&H&\\&|&\\H{-}&C&{-}H\\&|&\\&H&\end{matrix}$. This hydrocarbon is the lowest member of the paraffin series of hydrocarbons, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, etc. It will be noticed that the general formula for the series is C_nH_{2n+2}, where n represents the number of carbon atoms. The difference between two successive members of the series is CH_2.

Hydrocarbons of the Methane Series

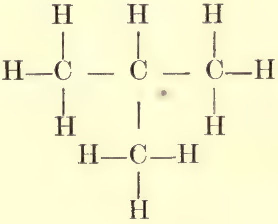
Name	Formula	Molecular Weight	Boiling Point	Freezing (or Melting) Point	
Methane	CH_4	16	– 160° C.	——	Ordinarily gaseous
Ethane	C_2H_6	30	– 93	——	
Propane	C_3H_8	44	– 45	——	
Butane	C_4H_{10}	58	+ 1	——	
Isobutane	C_4H_{10}	58	– 11	——	
Pentane	C_5H_{12}	72	36	——	Liquid
Decane	$C_{10}H_{22}$	142	173	– 32°	
Hexadecane	$C_{16}H_{34}$	226	287	+ 18	Solid
Octodecane	$C_{18}H_{38}$	254	317	28	

Two substances having the formula C_4H_{10} — butane and isobutane — are known. Graphic formulas show why this is possible.



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

butane



isobutane

With the valence of carbon, four, and of hydrogen, one, there is only one arrangement of the atoms possible for methane, ethane, and propane. For butane two may be seen. Moreover, butane and isobutane differ in their properties (see table). For pentane, there are three different arrangements of the atoms possible. The more numerous the carbon atoms, the greater the possibilities in arrangement. Thus for the formula $C_{13}H_{28}$, 802 different hydrocarbons are possible. When it is realized that some of the hydrogen atoms are replaceable by radicals such as $—OH$, $—Cl$, $—Br$, $—SO_4$, $—NO_3$, etc., a still further multiplication of the number of possible arrangements becomes evident. Hence the *arrangement of atoms in the molecule* is still another factor in accounting for the almost numberless carbon compounds. The graphic formulas are simply convenient means of representing the relations and probable arrangements of the atoms in the molecule.

185. Paraffin Series. — Methane, CH_4, is the simplest member of the paraffin series of hydrocarbons. It is the chief constituent of natural gas. Paraffin is derived from two Latin words, meaning "small affinity," thus characterizing the chemical inertness of these hydrocarbons. They are inactive with concentrated nitric and sulphuric acids, and resist the action of alkalies and most oxidizing agents. Paraffin is also the name for a white wax of common household and industrial use. It contains several of the higher members of the paraffin series. Petroleum (§ 360) consists of a mixture of various members of the paraffin series.

186. Methane, CH_4, is the simplest, but most important member of the paraffin series. It is the only hydrocarbon containing but one carbon atom.

This gas is formed by the decomposition of many organic compounds. As this action takes place in vegetable matter immersed in the stagnant water of marshes, methane is known as *marsh gas*. The bubbles which rise to the surface when such stagnant waters are stirred, consist mostly of marsh gas, but also contain some carbon dioxide and nitrogen.

In coal mines, methane is known as *fire damp*, because of its inflammable properties when mixed with air. Natural gas contains over 90% of methane.

The usual laboratory method of making methane is by a dry distillation of a mixture of soda lime and sodium acetate:

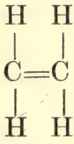
$$\underset{\substack{\text{sodium}\\\text{acetate}}}{NaC_2H_3O_2} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{NaOH} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\substack{\text{sodium}\\\text{carbonate}}}{Na_2CO_3}$$

Soda lime is a mixture of quicklime and caustic soda.

Methane is a colorless, odorless gas, a little more than half as heavy as air. It is slightly soluble in water. Like the other members of the paraffin series, it is a very stable compound, resisting the action of the strong acids and alkalies and even that of oxidizing agents. The action of methane with the halogens will be treated in § 190. The kindling temperature of methane is higher than that of hydrogen and its high heat of combustion makes it a valuable constituent of fuel gases. The equation for the complete combustion of methane is:

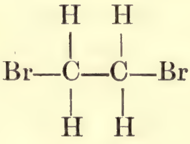
$$\underset{\text{methane}}{CH_4} + \underset{\text{oxygen}}{2O_2} \longrightarrow \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2} + \underset{\text{water}}{2H_2O}$$

187. Unsaturated Hydrocarbons. — In the paraffin hydrocarbons, we saw that the carbon atoms were joined by single bonds. There are other series, however, whose formation depends upon the fact that adjacent carbon atoms are joined by two or more bonds. The compounds in such a series are said to be *unsaturated.* Ethylene, C_2H_4, is the simplest unsaturated carbon compound. In such unsaturated compounds, it is believed that two adjacent carbon atoms are connected by a double bond, because an atom of a halogen element, like bromine, can be added to each, without the replacement of hydrogen. The graphic formulas of ethylene and ethylene dibromide represent this:



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

ethylene



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ Br & — & C & — & C & — & Br \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethylene dibromide

188. Ethylene Series. — This series of unsaturated hydrocarbons is represented by the general formula C_nH_{2n}.

Name	Formula	Boiling Point
Ethylene	C_2H_4	– 103° C.
Propylene	C_3H_6	– 48.5°
Butylene	C_4H_8	– 5.0°
Amylene	C_5H_{10}	+ 35°

Chemists have been unable to prepare the theoretical methylene, CH_2, which would be the first member of the series.

Ethylene, the most important member of the series, is formed by the destructive distillation of non-volatile organic compounds. It is found in natural gas, coal gas, and enriched water gas. The luminosity of illuminating gas is largely due to the 3 % or 4 % of ethylene they contain. Ethylene is more reactive than ethane, the corresponding member of the paraffin series, and has a lower kindling temperature. It was formerly called *olefiant* gas, which means "oil-forming." This was because of the fact that ethylene gives an oily liquid when it reacts with chlorine.

189. Acetylene Series. — In this series of hydrocarbons, two of the adjacent carbon atoms are joined by a triple bond, and the general formula is C_nH_{2n-2}. The first and only important member of the series is acetylene, C_2H_2, and its graphic formula is $H-C\equiv C-H$. The preparation and uses of this compound have already been discussed in §§ 99 and 119. Acetylene is also formed in small quantities in the incomplete combustion which takes place when a bunsen burner strikes back. The odor noticed at such times, however, is due to other gaseous products.

SUBSTITUTION PRODUCTS

190. Formation. — Chlorine, bromine, and iodine (halogen elements) react with methane to form compounds by the element replacing one or more hydrogen atoms in the hydrocarbon. The reaction between methane and chlorine is so violent that it is necessary to regulate it by having the reaction take place in diffused sunlight, or by diluting the mixture of the two combining gases with some inert gas such as carbon dioxide. The substitution products are named according to the number of halogen atoms replacing the hydrogen. Thus from chlorine and methane, CH_4, are formed:

CH_3Cl, monochlormethane
CH_2Cl_2, dichlormethane
$CHCl_3$, trichlormethane
CCl_4, tetrachlormethane

Similarly, bromine forms the brom-methanes, CH_3Br, CH_2Br_2, $CHBr_3$, and CBr_4.

Although many of the chlorine and bromine compounds may be formed by direct substitution, indirect methods are often more practical. The iodine substitution products of methane, CH_3I, CH_2I_2, CHI_3, and CI_4, are always made by indirect methods.

From the large number of hydrocarbons known, it is possible to obtain numerous halogen substitution products; few of them, however, are of practical importance. The more useful of these are described in the sections that follow.

191. Monochlormethane or Methyl Chloride. — This compound, CH_3Cl, is a colorless gas with an ethereal odor. It is easily liquefied under atmospheric pressure at − 24° C. The liquid is sometimes used in minor surgical operations, as its rapid evaporation deadens sensibility by chilling the affected part.

192. Chloroform or Trichlormethane, $CHCl_3$, was first made on a large scale by distilling a water solution of alcohol with bleaching powder. Now it is generally obtained commercially by distilling acetone with bleaching powder.

Chloroform is a heavy, volatile liquid, boiling at 61° C., but it is not inflammable. It has a sweet taste and a characteristic ethereal odor. While it is only slightly soluble in water, it is miscible with most of the organic solvents. Chloroform decomposes slowly when exposed to light and air, giving products that are more poisonous than the chloroform. To prevent this decomposition, commercial chloroform usually contains 1 % of ethyl alcohol.

The use of chloroform as an anæsthetic has diminished, as ether is safer in many cases. Chloroform is an excellent cleansing agent, but its principal use is as a solvent for organic compounds. Rubber is dissolved by it.

193. Iodoform, CHI_3, is a light yellow powder with a distinctive odor. It is made by adding iodine to a warm aqueous solution of ethyl alcohol, made alkaline with sodium hydroxide or sodium carbonate. The iodoform separates out as a yellow precipitate. This reaction is often used as a test for ethyl alcohol, but is not reliable when certain other organic compounds, as acetone, are present, since these compounds give the same result.

The antiseptic properties of iodoform led to its use in surgical dressings. To hide the disagreeable and pervasive odor, iodoform is generally put up in some mixture. "Eka-iodoform" contains iodoform and paraformaldehyde; "amozel," iodoform and thymol. "Di-iodoform" is tetra-iodo-ethylene, C_2I_4.

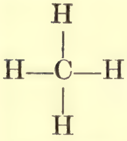
194. Carbon Tetrachloride, CCl_4, is the final result of the chlorination of methane (§ 190). It is made commercially by the action of chlorine on carbon disulphide, in the presence of antimony pentasulphide, Sb_2S_5, which is not permanently changed in the reaction :

$$\underset{\text{carbon disulphide}}{CS_2} + \underset{\text{chlorine}}{3\,Cl_2} \longrightarrow \underset{\text{carbon tetrachloride}}{CCl_4} + \underset{\text{sulphur chloride}}{S_2Cl_2}$$

Carbon tetrachloride is a heavy liquid, boiling at 77° C., and has an odor not unlike that of chloroform. It readily dissolves greases, gums, and resins. As a non-combustible solvent, the tetrachloride finds wide use in technical and manufacturing operations. Mixed with gasoline or benzine, it is sold as a cleaning fluid under various trade names, such as "Carbona." Such mixtures are non-inflammable. Tetrachloride is the important constituent of the fluid in some small portable fire extinguishers, for example "Pyrene."

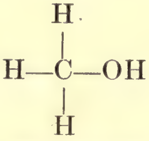
ALCOHOLS

195. General Characteristics. — The alcohols are hydroxyl derivatives from the hydrocarbons. They may be made by the substitution of one or more hydroxyl groups for a corresponding number of hydrogen atoms in a hydrocarbon. As a rule, two hydroxyl groups do not become attached to one carbon atom. The substitution is not a direct one, however, as it requires two steps. The common alcohols are not obtained commercially in this way.



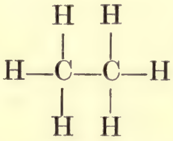
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

methane



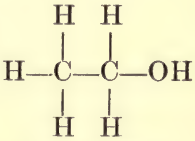
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & OH \\ & & | & & \\ & & H & & \end{array}$$

methyl alcohol



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethane



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethyl alcohol

The group CH_3^- (*methyl*) occurs in many carbon compounds, as does *ethyl*, $C_2H_5^-$. In other words, these groups are organic radicals and the recognition of these radicals aids greatly in naming many carbon compounds. Among other radicals of this class of frequent occurrence are: *propyl*, $C_3H_7^-$; *butyl*, $C_4H_9^-$; and *pentyl or amyl*, $C_5H_{11}^-$.

The alcohols show many resemblances to the metallic hydroxides or bases, but the basic properties of the alcohols are not so well marked. Although they combine with acids to form salts, the combination takes place slowly, and often special means, such as increase in temperature, have to be employed to effect the union. Moreover, in water solution the alcohols are not ionized sufficiently to affect litmus paper.

In the inorganic bases, the metal is combined with one or more hydroxyl groups, as $NaOH$, $Ca(OH)_2$, and $Fe(OH)_3$. In the case of organic bases, the organic radical is combined with hydroxyl, as CH_3OH, C_2H_5OH, and $C_3H_5(OH)_3$. Such organic radicals as methyl, CH_3^-, ethyl, $C_2H_5^-$ and glyceryl, $C_3H_5^-$, because of their positive (basic) nature, are termed *alkyl* radicals or groups. R is a general symbol used for an alkyl radical. The general formula for an alcohol is $R-OH$.

196. Methyl or Wood Alcohol, CH_3OH, is obtained commercially by the destructive distillation of wood (§ 367). It is a colorless liquid with a distinctive odor and boils at 66°. Not only does it mix readily with water in all proportions, but it dissolves many other substances.

The solvent action of wood alcohol is used in the preparation of many shellacs and varnishes. It burns with a clean flame of high heat value, and is suitable for use in the spirit lamps of curling irons and chafing dishes. Crude wood spirit is used for denaturing grain alcohol. Methyl alcohol is useful in the preparation of formaldehyde, aniline dyes, and many other organic compounds.

Wood alcohol is a deadly poison. In confined and poorly ventilated places, even the fumes of it have caused fatal prostration among men using varnishes containing it. Paralysis of the optic nerve is one effect of wood alcohol poisoning. Many cases of total blindness have been caused by the drinking of cheap whiskies adulterated with wood alcohol. Even its use in bathing is dangerous.

197. Ethyl or Grain Alcohol, C_2H_5OH, is a product obtained from the fermentation of sugars. Among the fermentable sugars are *sucrose* or cane sugar, found in the sugar cane and in the sugar beet; *dextrose* and *levulose* (fructose) which occur in fruits and vegetables. Dextrose is commonly known as grape sugar, on account of its occurrence in grapes. Although dextrose and levulose have the same formula, $C_6H_{12}O_6$, they are different compounds, as the atoms are arranged differently in their molecules. A very important sugar for making alcohol is *maltose*, $C_{12}H_{22}O_{11} \cdot H_2O$. This sugar is obtained from starch by the action of *diastase*, a substance produced in fermentation, which acts as a catalytic agent. In this country, alcohol is made largely from the starch contained in corn, rye, or barley. Abroad, potatoes and molasses are more widely used. Diastase is contained in malt, which is prepared by allowing barley to sprout in a warm, moist atmosphere, and then heating the sprouted grain to stop its growth.

The technical preparation of alcohol takes place in the following steps:

(1) The grain is ground, after it has been heated in order to burst the covering of the starch granules. Then it is mixed with a small amount of malted grain.

(2) The diastase in the malt converts the starch into maltose:

$$\underset{\text{starch}}{2\,C_6H_{10}O_5} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{maltose}}{C_{12}H_{22}O_{11} \cdot H_2O}$$

The malted mixture is agitated meanwhile with water at 63° C., as this is the best temperature for the conversion.

(3) The liquid is then cooled, diluted with water, and yeast added. Yeast is a microscopic vegetable organism growing in chains of oval-shaped cells (Fig. 77). During the process of its growth, the yeast forms a ferment known as *zymase*. This, acting as a catalytic agent, brings about the following reaction:

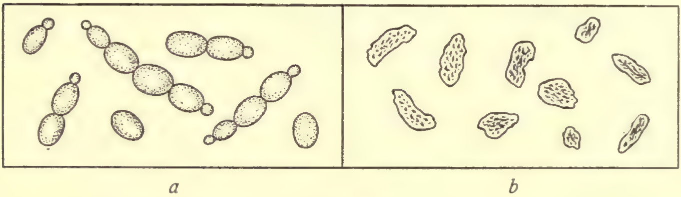


FIG. 77.—YEAST CELLS, HIGHLY MAGNIFIED: *a*, living; *b*, dead.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11} \cdot H_2O} \longrightarrow \underset{\text{alcohol}}{4\,C_2H_5OH} + \underset{\text{carbon dioxide}}{4\,CO_2}$$

This fermentation takes from three to nine days and occurs best in a solution containing about 10% sugar.

(4) The fermented liquid, containing from 10% to 13% of alcohol, is distilled or rectified in an apparatus so efficient that two distillations yield an alcohol containing but 5% of water.

When molasses (cane sugar) is used, the process is similar, except that no malt is necessary. The cane sugar is first converted into dextrose and levulose by a ferment also produced by the yeast plant, known as *invertase:*

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}$$

Then the zymase from the yeast brings about the alcoholic fermentation of the two simple sugars:

$$\underset{\substack{\text{dextrose or}\\ \text{levulose}}}{C_6H_{12}O_6} \longrightarrow \underset{\text{alcohol}}{2\,C_2H_5OH} + \underset{\text{carbon dioxide}}{2\,CO_2}$$

198. Properties of Ethyl Alcohol. — This alcohol is a colorless liquid of characteristic odor, with a specific gravity four fifths that of water. It is miscible with water in all proportions, the mixing being attended with contraction of volume and the evolution of some heat.

Ordinary alcohol contains 5 % by volume of water. This is because the process of fractional distillation of dilute alcohol does not yield an alcohol more concentrated than 95 %, since this is a constant boiling mixture.

Alcohol is a poison, although small quantities can be taken into the body, where it is oxidized and produces heat.

199. Uses of Ethyl Alcohol. — Alcohol has many minor uses in the household. On account of its rapid evaporation, it is used extensively to reduce the temperature of feverish patients. Its solvent power leads to a wide range of uses. Pharmacists find it invaluable in the preparation of tinctures, essences, extracts, and many medicinal preparations. Many of the better grades of shellacs and varnishes contain ethyl alcohol. The use of alcohol in beverages consumes large quantities.

Among the chief industrial uses are the manufacture of vinegar, iodoform, chloroform, and many other organic compounds. A coming use is for internal combustion engines, as present indications are that there will not be enough gasoline to meet all demands.

200. Denatured Alcohol is ethyl alcohol to which wood alcohol or other poisonous substances have been added, in order to make its use for beverages or medicines impossible. The internal revenue tax is $1.10 per gallon of proof spirit, which is 50 % alcohol. This makes a tax of about $2.00 for the 95 % alcohol. Denatured alcohol is tax free, so as to encourage its industrial use.

Completely denatured alcohol, as authorized by the government, contains:

100 parts ethyl alcohol (not less than 90% strength),
10 parts methyl (wood) alcohol,
$\frac{1}{2}$ part benzine.

There are also other formulas for special purposes which may be made under government license.

201. Alcoholic Beverages. — These may be classed as (1) the direct products of fermentation, as beer, wines, and champagnes, and (2) distilled liquors, in which the fermented products are distilled to increase the percentage of alcohol.

Beer is made by the fermentation of malt, prepared as described in §197. The temperature is kept down to 5° C. by refrigeration. The yeast grows at the bottom of the vat. The fermented liquor is filtered, hops added to give a bitter taste and keeping qualities, and then water added to the desired concentration. Beer contains from 3% to 5% of alcohol. Rice and glucose are often used to replace the barley. In making *ale*, the yeast grows at the top of the fermenting liquid, which is kept at about the ordinary temperature. Ale contains from 3% to 8% of alcohol.

Wines are made by the fermentation of sugars in fruit juices, particularly those of the grape. Various ferments are peculiar to different wine-producing regions. The wine is kept for some time to allow the tannin and other substances to precipitate, as well as to allow certain other compounds to react and produce substances which give an agreeable flavor. Claret, Rhine wines, and sauternes contain from 7% to 12% of alcohol. Port, sherry, and Madeira contain from 15% to 20%. These last three wines are generally fortified, that is, alcohol is added to the fermented liquid to obtain the desired percentage. Fermentation does not give more than 17% alcohol, as at that concentration the yeast cells are killed.

Champagne is made by conducting the fermentation in corked bottles, the process taking from 6 months to 2 years. The bottles are tilted mouth downwards, so that the sediment will collect in the neck. Finally the bottle is opened for a moment, in order to blow out the sediment. Next a little sugar solution is added to fill the bottle, which is then corked and stored until the champagne is deemed to have a uniform composition. The alcohol content is from 8% to 11%. Imitation champagnes are made by saturating white wines with carbon dioxide under pressure.

Whisky is made by distilling a beer made from rye, corn, or barley. It is stored in wooden barrels until the desired flavor is obtained and the fusel oil disappears. Fusel oil is chiefly a mixture of the two amyl alcohols $C_5H_{11}OH$. Whisky contains from 25% to 45% of alcohol, and gets its flavor from materials in the malted grain and from the wooden kegs in which it is stored.

Brandy is made by distilling wine, or the fermented juices of apples, peaches, cherries, or other fruits. It contains from 40% to 50% of alcohol. *Gin* is prepared by the distillation of an alcoholic liquor made from grain. The final distillation takes place with juniper berries or anise seed, so as to get the characteristic flavor. Gin usually contains about 30% of alcohol. *Rum* is made by distilling the liquid obtained by fermenting molasses. The percentage of alcohol contained varies from 40% to 80%. *Liqueurs* or *cordials* are made by steeping fruits or aromatic herbs in alcoholic liquors and then distilling. Sirup is then added to the product, and often coloring matter as well.

SUMMARY

Hydrocarbons are compounds containing only hydrogen and carbon.

Paraffin Series of Hydrocarbons have the general formula C_nH_{2n+2}. Methane, CH_4, is the simplest member of this series.

Unsaturated Series of Hydrocarbons are typified by the *ethylene* series, C_nH_{2n}, and the *acetylene* series, C_nH_{2n-2}. Acetylene, C_2H_4, is the first member of the latter series.

Substitution Products of hydrocarbons are formed by the replacement of one or more hydrogen atoms by a corresponding number of atoms of such elements as chlorine, bromine, and iodine. Chloroform, $CHCl_3$, and iodoform, CHI_3, are important substitution products.

Alcohols are hydroxyl derivatives of the hydrocarbons. They consist of some such alkyl radical as methyl, CH_3^-, or ethyl, $C_2H_5^-$, in union with one or more hydroxyl groups. Important alcohols are methyl or *wood alcohol*, CH_3OH, ethyl or *grain alcohol*, C_2H_5OH, and *glycerin*, $C_3H_5(OH)_3$. Alcohol results from the conversion by fermentation of a sugar into an alcohol and carbon dioxide.

Denatured Alcohol is grain alcohol rendered unfit for beverages and medicines by the addition of some poisonous substance, as wood alcohol or benzine.

EXERCISES

1. Give two reasons for the number and complexity of carbon compounds.

2. Write the graphic formulas for the three possible pentanes, C_5H_{12}.

3. What is marsh gas? Fire damp?

4. What is an unsaturated hydrocarbon? Give the name and graphic formula for one.

5. Write an equation for the preparation of acetylene.

6. Give the name, formula, and an important use of each of three halogen substitution products.

7. What are the advantages of carbon tetrachloride as a cleaning fluid?

8. What is an alkyl radical? Give names and formulas for two common ones.

9. What are alcohols? How do they differ from inorganic bases?

10. Why should varnishes made with wood alcohol have this fact printed on the container?

11. State the catalytic action brought about by each of the following: diastase, invertase, and zymase.

12. Write two equations showing the formation of ethyl alcohol from (*a*) starch, (*b*) cane sugar.

13. How is alcohol obtained from fermented liquids?

14. Show how the properties of ethyl alcohol lead to its important uses.

15. What is denatured alcohol? Why is it made?

CHAPTER XX

CARBON COMPOUNDS

Aldehydes, Acids, Esters, and Carbohydrates

ALDEHYDES

202. Characteristics. — Aldehydes are made by removing two hydrogen atoms from an alcohol. The name aldehyde is derived from this process (*al*cohol *dehyd*rogenatus).

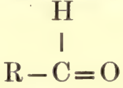
The removal of the hydrogen is accomplished by oxygen, hence aldehydes are *oxidation products of alcohols.* Thus, methyl alcohol is oxidized to formaldehyde:

$$\underset{\text{methyl alcohol}}{CH_3OH} + \underset{\text{oxygen}}{O} \longrightarrow \underset{\text{formaldehyde}}{HCHO} + \underset{\text{water}}{H_2O}$$

Further oxidation changes an aldehyde to an acid, the aldehyde taking its name from the acid into which it oxidizes. The following shows the relations of the two simplest aldehydes:

$$\begin{array}{llll} CH_3OH & \text{methyl alcohol} & C_2H_5OH & \text{ethyl alcohol} \\ & \text{oxidizes to} \downarrow & & \text{oxidizes to} \downarrow \\ HCHO & \text{formaldehyde} & C_2H_5CHO & \text{acetic aldehyde} \\ & \text{oxidizes to} \downarrow & & \text{oxidizes to} \downarrow \\ HCOOH & \text{formic acid} & C_2H_5COOH & \text{acetic acid} \end{array}$$

An aldehyde does not contain a hydroxyl group. The general formula for aldehydes shows this:



$$\begin{array}{c} \phantom{R-{}}H \\ \phantom{R-{}}| \\ R-C=O \end{array}$$

R stands for an alkyl radical, as methyl, CH_3-, ethyl, C_2H_5-, etc.

203. Formaldehyde. — This simplest aldehyde is made practically by burning methyl alcohol in a limited supply of air. The air is drawn through methyl alcohol warmed to about 45°. The mixture of air and alcohol vapor then passes over a heated copper spiral. Soon the heat of the reaction producing the formaldehyde keeps the copper hot enough to bring about the oxidation of the alcohol vapors. The gases are condensed to a liquid containing formaldehyde, water, and some methyl alcohol. By proper regulation, a solution containing 40% formaldehyde can be made by this process. The product is known as *formalin.*

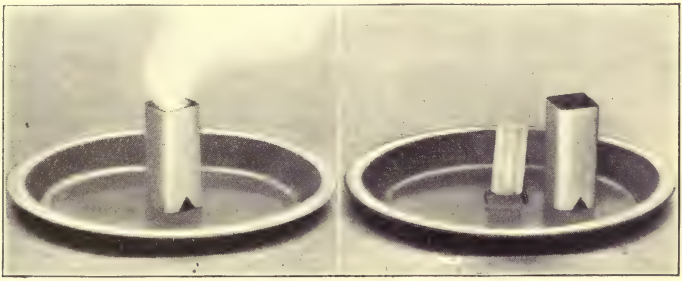


Fig. 78.

Formaldehyde candle for fumigation. Box removed to show candle.

Formaldehyde is a gas with a stinging, stifling odor, and causes the eyes to smart. It liquefies at − 21° C. Both the moist gas and its water solution are powerful germicides. Specially constructed lamps for burning methyl alcohol in an insufficient supply of air were used for producing formaldehyde for disinfection. Tablets, or candles, of formacone (Fig. 78) are now generally used. *Formacone* is a white, crystalline solid, made by heating the water solution of formaldehyde, or by evaporating the solution with sulphuric acid. A number of formaldehyde molecules unite to form the complex molecule $(HCHO)_x$

of formacone, whose structure is not known. When formacone is heated, or boiled with water, formaldehyde is evolved.

Sometimes in public places small quantities of formalin are sprayed into the air. More frequently, specially devised machines continually furnish small amounts of formaldehyde gas to the air, as a deodorizer and disinfectant. Formaldehyde does not produce the undesirable bleaching effect of sulphur dioxide, when used for fumigation.

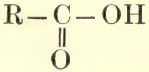
Among other uses of formaldehyde are the preservation of anatomical specimens, the hardening of gelatin films for photographic plates, and the objectionable employment as a food preservative.

ORGANIC ACIDS

204. Characteristics. — As shown in § 202, the oxidation of an alcohol gives an aldehyde. Further oxidation changes the aldehyde to an acid. The organic acids, then, are oxidation products of the alcohols. Thus, acetic acid is made from ethyl alcohol. A comparison of the formulas shows that one oxygen atom has replaced two hydrogen atoms:

$CH_3 . CH_2OH$ ethyl alcohol (C_2H_5OH)
$CH_3 . COOH$ acetic acid ($HC_2H_3O_2$)

The introduction of the oxygen atom gives an acid character to the molecule formed. The group $-COOH$ is known as *carboxyl*. The organic acids may be regarded as carboxyl derivatives of the hydrocarbons. The union of an alkyl radical, like methyl or ethyl, with hydroxyl gives an alcohol, a substance with properties resembling a base. An alkyl radical with carboxyl gives an organic acid. The organic acids have many properties in common with the inorganic acids, but are much less active as a class. They have the general formula:



$$\mathrm{R-\underset{\underset{O}{\|}}{C}-OH}$$

205. Fatty Acids. — The acids containing but one carboxyl group, and derived from the paraffin series of hydrocarbons, are known as fatty acids. Some of those first isolated were obtained by the decomposition of certain fats.

Some Fatty Acids

Name	Formula	Melting Point	Occurrence
Formic acid .	$H.COOH$	8.3° C.	Red ants
Acetic acid .	$CH_3.COOH$	16.6° C.	Sorrel; fruit juices
Propionic acid	$C_2H_5.COOH$	– 36° C.	
Butyric acid .	$C_3H_7.COOH$	– 2° C.	Rancid butter
Valeric acid .	$C_4H_9.COOH$	– 58.5° C.	Valerian wood
Caproic acid .	$C_5H_{11}.COOH$	– 1.5° C.	Rancid coccanut oil
Palmitic acid .	$C_{15}H_{31}.COOH$	62.6° C.	As salts (esters) in animal and vegetable oils and fats
Margaric acid	$C_{16}H_{33}.COOH$	60° C.	
Stearic acid .	$C_{17}H_{35}.COOH$	963° C.	

206. Acetic Acid. — Acetic acid,

$$H(C_2H_3O_2) \text{ or } CH_3COOH,$$

is obtained in quantity from the destructive distillation of wood (§ 367). *Commercial* acetic acid is a liquid which contains 50% of $H(C_2H_3O_2)$. *Glacial* acetic acid contains less than 1% of water. When it is pure, it boils at 119° C., and solidifies at 16.6° to an icelike solid, to which fact it owes its name. The glacial acid has a very penetrating odor and is an excellent solvent for many organic salts.

Acetic acid can also be obtained by the oxidation of grain alcohol:

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{acetic acid}}{HC_2H_3O_2} + \underset{\text{water}}{H_2O}$$

The reaction is brought about in dilute alcohol solutions by acetic acid bacteria (Fig. 79) (mother of vinegar) in the presence of oxygen from the air. By this *acetic acid fermentation*, vinegar is made from dilute solutions of alcohol, as wine, cider, or the liquid from fermented malt. The process takes several weeks, as the absorption of oxygen takes place at the surface of the liquid only. The vinegar obtained contains from 6% to 10% of acetic acid, as well as certain natural coloring and flavoring materials.

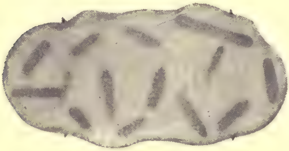


FIG. 79. — ACETIC ACID BACTERIA. (Magnified 4000 diameters.)

In the *quick vinegar process*, a solution containing about 10% alcohol is allowed to trickle over beech wood shavings loosely filling large vats, through which air circulates. The shavings are first drenched with old vinegar, so as to insure the presence of the fermenting organism. The process takes about ten days and the product contains from 4% to 6% of acetic acid. As the vinegar obtained is often a colorless liquid, coloring and flavoring materials are added.

ESTERS OR ETHEREAL SALTS

207. Formation. — Esters are an important class of organic compounds. They occur widely distributed in nature, giving the characteristic odors to many flowers and fruits. Many of the esters are readily volatile liquids, a fact which suggested the name *ethereal salts*. Banana oil, often used in aluminum paint, is amyl acetate; oil of wintergreen is methyl salicylate.

Esters are formed by a reaction corresponding to the formation of an inorganic salt by neutralization:

$$\overset{\textit{base}}{\underset{\substack{\text{potassium}\\ \text{hydroxide}}}{\mathrm{KOH}}} + \overset{\textit{acid}}{\underset{\text{nitric acid}}{\mathrm{HNO_3}}} \longrightarrow \overset{\textit{salt}}{\underset{\substack{\text{potassium}\\ \text{nitrate}}}{\mathrm{KNO_3}}} + \overset{\textit{water}}{\mathrm{HOH}}$$

$$\overset{\textit{alcohol}}{\underset{\text{ethyl alcohol}}{\mathrm{C_2H_5OH}}} + \overset{\textit{acid}}{\underset{\text{nitric acid}}{\mathrm{HNO_3}}} \rightleftarrows \overset{\textit{ester}}{\underset{\text{ethyl nitrate}}{\mathrm{C_2H_5NO_3}}} + \overset{\textit{water}}{\mathrm{HOH}}$$

This reaction of an alcohol and an acid to produce an ester and water is termed *esterification.* Unlike a true neutralization, the reaction proceeds slowly at ordinary temperatures, but is accelerated by heating. As the reaction is a reversible one, it does not run to completion, unless some dehydrating agent, as concentrated sulphuric acid or hydrogen chloride, is present to take up the water formed. Esterification may be described as the reaction of an alcohol with an acid, brought about by the elimination of water.

208. Chemical Properties. — Although the esters resemble inorganic salts in the method of their formation, their chemical properties are quite unlike. Most of the inorganic salts are highly ionized (§ 406) and take part readily in reactions of double replacement. The esters are not ionized and their reactions are often different from those of double replacement. The esters resemble most closely the inorganic salts formed from a weak acid or a weak base. Like them, they are easily decomposed (hydrolyzed) with water:

$$\underset{\text{potassium cyanide}}{KCN} + \underset{\text{water}}{HOH} \rightleftarrows \underset{\text{potassium hydroxide}}{KOH} + \underset{\text{hydrocyanic acid}}{HCN}$$

$$\underset{\text{ethyl acetate}}{C_2H_5C_2H_3O_2} + \underset{\text{water}}{HOH} \rightleftarrows \underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic acid}}{H(C_2H_3O_2)}$$

In this hydrolysis, water splits the ester into the alcohol and acid from which it was formed. This process is *saponification* and is very important in soap making (§ 211). Saponification takes place most completely when the water is hot, under pressure, or in the presence of alkalies or acids.

209. Esters of Inorganic Acids. — The esters of the strong inorganic acids can be prepared by the action of the acid with an alcohol, although certain precautions are often necessary. The esters of the weak inorganic acids are prepared by special methods.

Among some of the well-known esters of inorganic acids are ethyl nitrite, $C_2H_5NO_2$, whose alcoholic solution is the medicinal "sweet spirits of niter"; amyl nitrite, $C_5H_{11}NO_2$, also used in medicine; and glyceryl nitrate, $C_3H_5(NO_3)_3$, which is more familiarly known as the explosive nitroglycerin. This is made from glycerin.

210. Hydrogenation of Oils. — The supply of lard for cooking purposes has not kept pace with the demand. Olive oil is too expensive a substitute, and cottonseed oil has certain objectionable qualities when so used. Hence the manufacture of substitutes for lard has become common. In making these, large quantities of the hard fat, stearin (§ 211), obtained as a by-product of the oleomargarine factories, have been used. Recently a method has been discovered for the hydrogenation of oils which are composed of unsaturated acids and their esters. Thus, oleic acid, in the presence of a suitable catalytic agent, will combine with hydrogen, forming a saturated compound:

$$\underset{\text{oleic acid}}{C_{17}H_{33}COOH} + \underset{\text{hydrogen}}{H_2} \longrightarrow \underset{\text{stearic acid}}{C_{17}H_{35}COOH}$$

By this process an oil is converted into a hard fat.

A number of catalytic agents have been tried, but thus far finely divided palladium and freshly reduced nickel have proved to be the most successful. The hydrogen is obtained electrolytically, or by passing steam over reduced, spongy iron. One per cent of hydrogen by weight converts cottonseed oil into a fatty body of the consistency of lard. The product obtained is edible.

Hydrogenation has also proved of great value to the soap industries. Oils which formerly gave soft soaps are now converted into compounds which yield the more valuable hard soaps. Fish oil and whale oil, which have objectionable odors, are converted into deodorized oils suitable for soap making.

The hydrogenation of oils is a rapidly developing industry. By it, animal and vegetable oils can be converted into fatty bodies of any desired consistency, as the process admits of a high degree of control. Its products are not only valuable to soap makers and lard manufacturers, but are also useful in the making of lubricants and other technical products.

211. Glycerin, $C_3H_5(OH)_3$, is an alcohol obtained from certain animal fats and vegetable oils. These are mixtures of palmatin, stearin, and olein, which may be considered as esters made from the alcohol, glycerin, and palmitic acid ($C_{15}H_{31} . COOH$), stearic acid ($C_{17}H_{35} . COOH$), and oleic acid ($C_{17}H_{33} . COOH$), respectively. A preponderance of stearin gives the harder fats, as beef and mutton tallows, while a large proportion of olein occurs in lard, olive oil, and cottonseed oil. Palm oil is chiefly palmatin.

Glycerin results from the hydrolysis of the glyceryl (C_3H_5) esters, the water splitting the ester into an alcohol and an acid (§ 208):

$$\underset{\text{glyceryl stearate}}{(C_{17}H_{35}\cdot COO)_3C_3H_5} + \underset{\text{water}}{3\ HOH} \rightleftarrows \underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3\ C_{17}H_{35}\cdot COOH}$$

This reaction is carried out on a commercial scale by heating the glyceryl stearate and water under pressure in the presence of a little lime. By this process large quantities of glycerin are made. The other valuable product of the reaction, stearic acid, is used for making soaps and candles.

Another important source of glycerin is soap making, as the hydrolysis of the glyceryl esters conducted in the presence of an alkali, yields a soap and glycerin. The process is termed ***saponification***. Common soap is a mixture of the sodium salts of the organic acids mentioned above. The reaction for the saponification of stearin is:

$$\underset{\text{glyceryl stearate}}{(C_{17}H_{35}\cdot COO)_3C_3H_5} + \underset{\text{sodium hydroxide}}{3\ NaOH} \rightleftarrows \underset{\text{sodium stearate}}{3\ C_{17}H_{35}\cdot COONa} + \underset{\text{glycerin}}{C_3H_5(OH)_3}$$

The glycerin is separated from the spent lye of the soap works. This liquid is run off, any excess of soap removed, certain impurities precipitated with iron salts, and the liquid evaporated, so as to cause the sodium chloride to crystallize out. Superheated steam is passed through the liquid residue, and carries the glycerin off with it. The distillate is evaporated in vacuum pans, to dispose of the excess of water. This last evaporation is continued until the liquid has a specific gravity of 1.26.

Glycerin is a sirupy liquid with a sweet taste. It is miscible with water and alcohol. Its solvent action approaches that of water, as it dissolves a great variety of substances. Glycerin is so hygroscopic that it will absorb half its weight of water from the moisture of the air.

Glycerin is widely and extensively used. Large quantities are converted into nitroglycerin. Glycerin is used in cosmetic and medicinal preparations, in the ink rolls of printers, and in the ink for rubber stamps. It is also used to keep tobacco moist and to soften leather. These uses are largely due to its hygroscopic properties.

212. Nitroglycerin, $C_3H_5(NO_3)_3$, is the trinitrate of glycerin, made by slowly adding glycerin to a mixture of fuming nitric and concentrated sulphuric acids, with the temperature kept below 20° C.:

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{nitric acid}}{3\ HNO_3} \rightleftarrows \underset{\text{nitroglycerin}}{C_3H_5(NO_3)_3} + \underset{\text{water}}{3\ HOH}$$

The sulphuric acid does not appear in the equation. Its dehydrating action causes the reaction to continue by absorbing the water formed. The nitroglycerin is drawn off from the nitrating mixture and is washed with water and then with a very dilute solution of sodium carbonate.

Nitroglycerin is a heavy, colorless, oily liquid, and freezes at about 8° C. It explodes when heated to 180° or when subjected to shock. For convenience in handling, it is absorbed by some inert, porous substance, such as infusorial earth, producing an earthy, powdery mass. The original dynamite of Nobel was made in this way. It is now sold under the name of 75% dynamite or No. 1

giant powder. The modern dynamites are more explosive. They contain about 13% wood pulp, 33% nitroglycerin, and 54% of some oxidizing agent, such as sodium nitrate. Sometimes the wood pulp itself is partly nitrated. Dynamites are classified and named according to the percentage of nitroglycerin they contain.

Gelatin dynamite, or blasting gelatin, is made by dissolving 1 part nitrocellulose (§ 214) in 9 parts nitroglycerin. This forms a clear jellylike mass resembling gelatin. As there is no inert matter, gelatin dynamite is a very powerful explosive. It is particularly useful for heavy blasting.

CARBOHYDRATES

The carbohydrates are an important class of compounds, composed of carbon, hydrogen, and oxygen. The hydrogen and oxygen in the molecule are in the same proportion by weight as they are in water.

213. Cellulose composes the cell walls of plants and is represented by the formula $(C_6H_{10}O_5)_x$. Absorbent cotton and washed filter paper are nearly pure cellulose. It is the main constituent of straw and wood. Cellulose may be obtained from vegetable fibers by several successive treatments with chlorine and sodium hydroxide, in order to convert the compounds associated with it into soluble ones that can be removed by washing.

Cellulose is soluble in Schweitzer's reagent, an ammoniacal solution of cupric hydroxide. The addition of hydrochloric acid precipitates the cellulose. *Waterproof paper* is prepared by leaving paper a short time in contact with Schweitzer's reagent, which acts upon the surface. Then the paper is passed through heated rolls and dried.

When unsized paper is left for a moment in contact with dilute sulphuric acid (1:4), it is converted into a colloidal cellulose known as *amyloid*. After washing with water and dilute ammonia, the paper becomes tougher and has a smoother surface. This product is known as *parchment paper*.

Although dilute alkalies hardly affect cellulose, boiling with more concentrated solutions of alkali cause vegetable cellulose fibers to become rounded and swollen and to assume a silky appearance. This is the process of mercerizing described in § 306.

214. Nitrocellulose is the earlier name given to a set of compounds which are now generally regarded as true nitrates of cellulose. They are made by replacing in cellulose from 2 to 6 hydroxyl groups by NO_3 groups. This is accomplished by a mixture of concentrated nitric and sulphuric acids. The degree of nitration of cellulose depends upon the concentration of the nitric and sulphuric acids, the temperature, the time of contact, and the relative mass of materials. The lower nitrates are known as *pyroxylin* and their solubility in a mixture of alcohol and ether decreases with the number of NO_3 groups introduced. *Collodion* is such a solution of pyroxylin. On the evaporation of the alcohol and ether, a tough, transparent film remains. On this account, collodion is used on photographic plates, for lacquers, and as a liquid court plaster. *Celluloid* is made by incorporating two parts of pyroxylin with one part of camphor. As the nitrocelluloses are explosive when heated, celluloid articles should not be thrown into the stove. Many serious accidents have been caused by doing this.

The treatment of dry cotton with concentrated nitric and sulphuric acids under certain conditions yields the hexanitrate, $[C_{12}H_{14}O_4(NO_3)_6]_x$, commonly known as *gun-*

cotton. The cellulose hexanitrate is the basis of many high explosives. It is insoluble in water, ether, or chloroform.

215. Smokeless Powder. — While wood pulp and paper may be used for making the cheaper explosives and cheap celluloid, cleaned and bleached cotton wool and the waste from cotton mills are employed in the making of guncotton for smokeless powders. After the nitrocellulose is prepared and washed free from acids, it is made into a plastic mass with the aid of a little ether-alcohol mixture. This dough is then run through a machine which presses it into perforated rods. The rods are cut into grains of a size suitable to the gun in which they are to be exploded. Finally the powder is very carefully dried, so as to reduce the amount of volatile matter (water, alcohol, and ether).

Acetone is sometimes used for working the cellulose nitrate into a pasty mass, and nitroglycerin and other nitro-organic compounds are incorporated during the making of the smokeless powder. Nitrocellulose powders with a nitroglycerin base are safer and more uniform in action than straight nitrocellulose powders. The latter, however, are less corrosive to the gun. The wide use of smokeless powders and the demand for celluloid and its allied articles, have made nitrocellulose manufacture one of the most extensive chemical industries.

216. Starch, $(C_6H_{10}O_5)_x$, occurs as granules in the cells of nearly all plants. Certain seeds and roots are particularly rich in this substance. The starch in seeds serves as nourishment for the young plant until the leaves and roots become developed sufficiently to draw plant food from the air and the soil.

The principal source of starch in the United States is corn, while in other countries potatoes and rice are the chief sources of supply. The general method of extraction from corn includes soaking, grinding, and washing the material in water and then filtering. In the last process, the finely divided starch passes through bolting cloth and is recovered from the water in which it is suspended. When dried, the starch contains about 10% of water.

Heating with water causes the starch granules to swell and burst their enveloping cellulose membranes, forming a gelatinous mass. Further heating makes some of the starch pass into solution. Soluble starch, however, is usually made by treating starch with cold dilute acid for several days.

Heating with dilute acids changes starch into dextrin, maltose, and glucose. The action of diastase on starch has already been discussed in the production of alcohol (§ 197). When dry starch is heated to 200°–250°C., it is converted into dextrin. A delicate test for starch is the so-called starch iodide, formed when the starch comes in contact with iodine. Doubt exists as to the nature and formula of this characteristic blue compound.

Starch is a valuable constituent of many foods. In laundry work, the heat of the iron converts some of the starch into dextrin, which gives a glossy finish to the fibers. Rice starch is used for finishing cotton cloth and is the chief constituent of the rice powder used as a cosmetic. Wheat starch gives a paste of good adhesive qualities. *Sago* is starch made from the pith of certain palm trees. *Tapioca* is prepared from cassava, a starch occurring in the roots of certain tropical plants. Great quantities of starch are converted into dextrin or into glucose.

217. Dextrin has a light brown color. Dextrin dissolves in water, forming a sticky liquid. This accounts for its use in adhesives like the mucilage on the back of postage stamps, as a thickener for colors in calico printing, and for tanning extracts.

218. Manufacture and Refining of Sugar. — Several sugars of commercial importance were discussed in connection with the production of grain alcohol (§ 197). Cane sugar or sucrose, $C_{12}H_{22}O_{11}$, occurs in sugar cane, sorghum, the sugar beet, sugar maple, and honey.

The juice from the sugar cane is pressed out by passing the cane through rolls, while it is obtained from beets by cutting them into small pieces and extracting with water. Either of the liquids thus obtained is treated with milk of lime, to precipitate the organic acids and to separate the albuminous substances. After using carbon dioxide, to precipitate out any excess of lime, the liquid is run through a filter press to take out the precipitated solids. The clarified juice is then evaporated in vacuum pans, to get rid of the excess of water, and the greater part of the sugar is allowed to crystallize out, leaving a residue of molasses. The mass of sugar crystals is dried by whirling it in a centrifugal machine. The product is brown sugar, a raw product which is generally refined before being placed on the market.

The raw sugar is dissolved in water and filtered through bone black in order to remove the coloring matters. The purified sirup is then concentrated in vacuum pans, run out into tanks, and allowed to crystallize, forming the granulated sugar of commerce. The size of the crystals depends upon the amount of stirring. Although the crystals of pure sugar have a pale yellow tint, people demand that sugar shall be a pure white. Accordingly, the sugar refiners add some blue pigment (ultramarine) to counteract the yellow color.

Cane sugar melts at 160° C. When kept at its melting point for a time and then allowed to cool, it solidifies to a transparent, amber-colored mass, called *barley sugar*. When cane sugar is heated to 210° C., it loses water and *caramel* is obtained. This is much used as a coloring and flavoring material. When cane sugar is boiled with dilute acids, it is converted into dextrose and levulose, forms of sugar which do not crystallize readily. For this reason vinegar is often added to candy that is to be pulled.

219. Ether, $(C_2H_5)_2O$, is a representative of the class of alkyl oxides. Its practical importance has so overshadowed the other oxides that its correct designation as ethyl ether is rarely heard.

Ether is made by the reaction of alcohol and concentrated sulphuric acid heated to about 135° C. The first step is the formation of ethyl sulphuric acid:

$$\underset{\text{alcohol}}{C_2H_5OH} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{ethyl sulphuric}\\ \text{acid}}}{C_2H_5HSO_4} + \underset{\text{water}}{HOH}$$

When more alcohol is slowly added and the above temperature maintained, the second step occurs:

$$\underset{\text{alcohol}}{C_2H_5OH} + \underset{\substack{\text{ethyl sulphuric}\\ \text{acid}}}{C_2H_5HSO_4} \longrightarrow \underset{\text{ether}}{(C_2H_5)_2O} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4}$$

The sulphuric acid thus regenerated changes more alcohol into ether and the process would go on indefinitely, if the sulphuric acid did not become too much diluted by the water formed in the first reaction. Because it is made with sulphuric acid, ethyl ether is sometimes sold under the name of sulphuric ether.

Ether is a light, mobile, and colorless liquid, with a very low boiling point (35° C.). It dissolves a wide variety of organic substances. Water and ether are slightly soluble in each other, while alcohol and ether are freely miscible.

Ether forms very explosive mixtures with air. Vessels containing it should never be heated over a gas flame. The anæsthetic effect of ether is well known. It has largely replaced chloroform for this purpose, as its effects can be more readily controlled.

220. Aromatic Series. — Benzene or benzole, C_6H_6, is the simplest member of another series of hydrocarbons, whose general formula is C_nH_{2n-6}. These hydrocarbons are more active chemically than those of the paraffin series. From the benzene hydrocarbons are prepared a wide range of carbon compounds, many of which are most useful as dyes, drugs, and photographic developers. As a number of these organic compounds have an agreeable and even a spicy odor, they are often designated as the aromatic series of carbon compounds. *Benzene* is obtained from the coal tar of illuminating gas manufacture. It is a light, colorless liquid, boiling at 80° C. and dissolves a wide range of carbon compounds. It is an inflammable liquid and burns with a smoky flame. Benz*e*ne, C_6H_6, should not be confused with benz*i*ne, which is a mixture of low boiling paraffin hydrocarbons, obtained from petroleum.

Like the paraffin hydrocarbons, the aromatic hydrocarbons are the basis of series of related compounds — substitution products, aldehydes, alcohols, acids, and esters. Thus, from benzene is derived a phenol or an aromatic alcohol, C_6H_5OH, more commonly known as *carbolic acid*, because its hydroxyl hydrogen may be replaced by active metals like sodium and potassium, forming phenolates. It is, however, one of the weakest of acids.

Carbolic acid is a white substance, crystallizing in long needles, and melting at 43° C. One part of carbolic acid dissolves in 15 parts of water, and the 5% solution is much used for disinfecting purposes. Although one of the best disinfectants, it is now less used than formerly as a surgical antiseptic. Carbolic acid has a corrosive action on the skin and mucous membranes. It is a deadly poison.

The acid corresponding to benzene is *benzoic acid*, C_6H_5COOH. Its sodium salt, *sodium benzoate*, has attracted wide attention on account of its questionable use as a food preservative.

Aniline, $C_6H_5NH_2$, is important as the parent substance of the almost numberless aniline dyes.

SUMMARY

Aldehydes are made from alcohols by the removal of two hydrogen atoms by oxidation. *Formaldehyde*, HCHO, is the simplest and most useful aldehyde.

Organic Acids are oxidation products of the alcohols. These acids are characterized by the carboxyl group, —COOH. Grain alcohol formed by fermentation may be changed by a second fermentation into acetic acid. *Vinegar* is a very dilute solution of acetic acid produced by the fermentation of fruit juices.

Esters or Ethereal Salts are formed by the reaction of an acid with an alcohol. As in the neutralization of an inorganic acid with a base, the other product is water.

Saponification is a hydrolysis in which water splits an ester into the alcohol and the acid from which the ester was formed. *Glycerin*, $C_3H_5(OH)_3$, is obtained from the saponification of certain animal fats and vegetable oils. It is a by-product in soap making.

Carbohydrates are a class of compounds consisting of carbon combined with hydrogen and oxygen in the same proportion by weight as these two elements exist in water. Cellulose, sugar, starch, and dextrin are important carbohydrates.

Ethers are alkyl oxides. Ether used as an anæsthetic is ethyl oxide $(C_2H_5)_2O$. It is an important solvent for fats.

Aromatic Series of hydrocarbons have the general formula C_nH_{2n-6}. Benzole, C_6H_6, is the simplest member. The benzole hydrocarbons yield many important derivatives valuable as dyes and drugs. These are often spoken of as coal-tar products, as many of them are made from the tar obtained in the destructive distillation of coal.

EXERCISES

1. How are aldehydes made? How does an aldehyde differ in composition from an alcohol?

2. How does a copper spiral lamp, burning wood alcohol, produce formaldehyde for fumigation?

3. What action takes place during the burning of a formaldehyde candle?

4. What is formalin? What are its uses?

5. What two radicals in combination constitute an organic acid? Give an example.

6. Why are the acids derived from the paraffin hydrocarbons often spoken of as "fatty acids"?

7. What is meant by acetic acid fermentation? Write the equation. What is glacial acetic acid?

8. Show the resemblances and differences between esterification and neutralization.

9. What is saponification? Write the equation for the saponification of (*a*) ethyl acetate, (*b*) glyceryl stearate.

10. How does the hardness of fats and oils differ with their composition?

11. Describe briefly two commercial methods for making glycerin.

12. What happens when a bottle of glycerin is left open to the air?

13. Why is concentrated sulphuric acid used in making nitroglycerin?

14. How does a carbohydrate differ in composition from a hydrocarbon?

15. What is pyroxylin? Collodion? Celluloid? Guncotton?

16. Distinguish between dextrose and dextrin.

17. Why should ether containers be tightly closed?

18. What is sucrose? Rock candy? Barley sugar? Caramel?

19. Distinguish between benzine and benzene.

20. What is a phenol? Name an important one and give its use.

CHAPTER XXI

FOODS

221. Purposes for which Food is needed in the Body. — Human beings, like all warm-blooded animals, need food to serve three distinct purposes in the body. These are:

(*a*) to build up or replace worn-out parts;

(*b*) to act as a fuel in keeping the body warmer than the surrounding air;

(*c*) to furnish energy to enable the animal to do mechanical work.

In the matter of his food, an animal is often compared to a steam engine which needs fuel to enable it to do mechanical work. But the analogy is only partly true, because the animal needs food for the further purpose of repair as the parts of his machinery wear out, and of keeping his body at the precise temperature at which it will best do its work.

222. Fundamental Sources of Food. — All food is derived indirectly from the carbon dioxide of the air, together with water and certain soluble salts that are taken from the soil. No animal is so constructed that he can use these substances directly. Plants, however, have this power, and animals obtain their food by eating either plants or animals that subsist on vegetable food.

223. Organic Compounds. — Plants, in feeding on carbon dioxide and water, build up in their bodies many different chemical compounds. These are so numerous and their structure is so complex that in discussing their connection with foods, we shall refer to them under class names, and not as individual compounds.

224. Elements Present in Food Substances. — The fundamental body substance is *protoplasm.* From it all the tissues of the organism are derived. The elements that it contains, therefore, represent all the elements which must be supplied to the body in the way of food. The chief elements in protoplasm are: carbon, hydrogen, oxygen, nitrogen (these are the four elements from which organic compounds are chiefly formed), with phosphorus, sulphur, iron, potassium, chlorine, calcium, and a few others in extremely small quantities.

Muscle tissue is composed chiefly of carbon, hydrogen, and nitrogen. *Fat* is composed of carbon, hydrogen, and oxygen. The rigid part of bones is calcium or magnesium phosphate and carbonate. Blood contains iron compounds; the teeth, in addition to calcium compounds, contain silicon and traces of fluorine.

225. Classification of Foods. — For the sake of convenience, foods are divided into four classes based on the different purposes they serve in the body. As with most classifications, however, the dividing lines are not sharply drawn, and a food that is set down in one class may serve the body in other ways. The four classes, the purposes that they serve, and foods typical of each are shown below in tabular form:

1. **Proteins.**

Composition.	Organic compounds very rich in nitrogen.
Purpose.	To replace worn-out muscle tissue.
Examples.	Lean meat, white of egg.

2. Fats.

Composition.	Carbon, hydrogen, and oxygen.
Purpose.	Partly to serve as fuel in producing body heat and body energy; they have a high value in this respect. Partly to form layers of protective tissue, and these layers also serve as a reserve storehouse of food to be drawn on in case of necessity.
Examples.	Butter, meat fat, olive oil.

3. Carbohydrates.

Composition.	Carbon, with oxygen and hydrogen in the same proportion as in water.
Purpose.	To supply body heat and body energy; they resemble fats in this respect. Their value in this way is about half that of fats. They also assist in building fats in the body.
Examples.	Starch, cane sugar, and other sugars.

4. Mineral Compounds.

Composition.	Do not contain carbon as a rule.
Purpose.	They are needed in small quantity to serve a great variety of uses.
Examples.	Common salt, the mineral salts of meat, and vegetable juices.

226. The Measure of Food Values. — Most articles of food contain compounds that represent the four classes of food substances. They differ, however, very widely in the proportion of protein, carbohydrate, and fat which they contain. Meat has no carbohydrate, and many of the vegetable foods contain very little protein. Milk comes the nearest of all food substances to containing all the food elements in the proportion in which they are needed in the body, but this food is not adapted to the needs of adult life. The rational diet should, therefore, consist of different foods used in such proportion that they meet all the needs of the body.

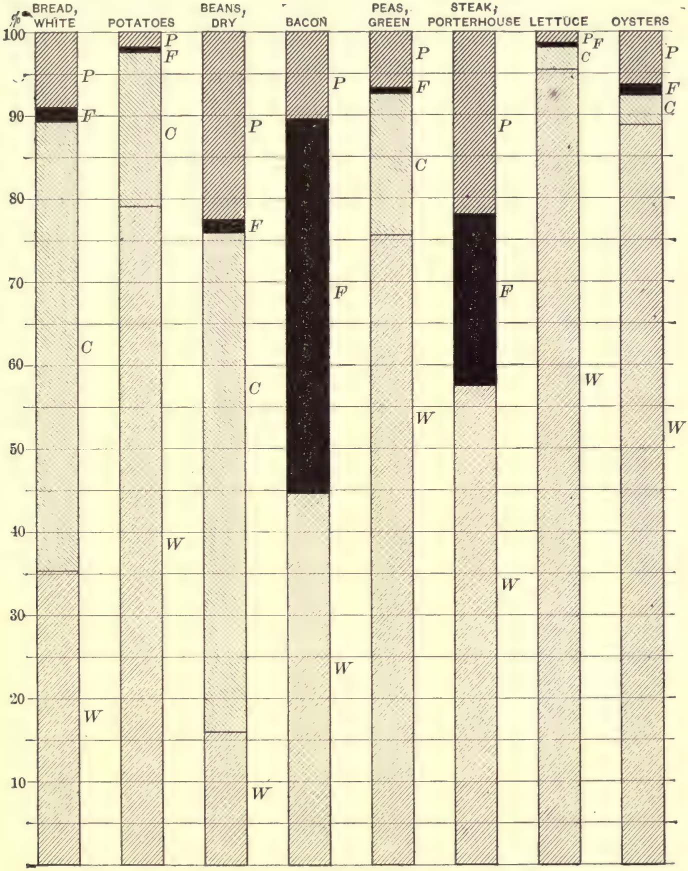


FIG. 80. — PERCENTAGE COMPOSITION OF COMMON FOODS
W, water; *C*, carbohydrates; *F*, fat; *P*, protein.

Since fats and carbohydrates serve practically the same purpose, that of supplying the organism with heat and muscular energy, it is found that the food values can be considered under three heads:

(*a*) nitrogen content,

(*b*) heat or energy value,

(*c*) the supply of mineral compounds.

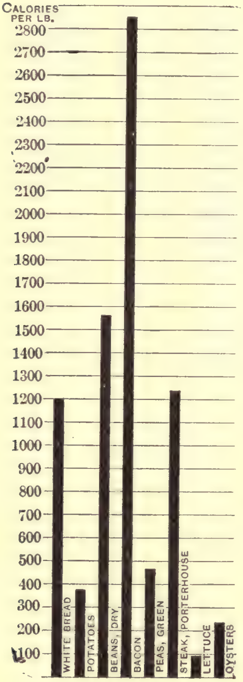


FIG. 81. — CALORIFIC VALUE OF FOODS.

The first of these is measured by the amount of protein matter present in the food. The second, which is derived chiefly, but not entirely, from the carbohydrates and fats, is determined by an instrument known as the combustion calorimeter. The results which it gives are expressed in units called *Calories.* A Calorie is the amount of heat necessary to warm a kilogram of water one degree Centigrade. The number of Calories furnished by a given food indicates the amount of heat liberated when it is completely oxidized. This is practically what happens to food when it is consumed in the body, since its hydrogen is finally converted into water, and its carbon into carbon dioxide. The number of Calories is a fair measure of the energy value (Fig. 81), because in the body, as in machinery, heat may be converted into mechanical work.

227. Quantity of Food Required. — The amount and character of food needed by the human being has been the subject of much discussion, and authorities are not in complete agreement. In recent years, however, much elaborate experimentation has been carried on and a great deal has been added to our store of knowledge.

Among the many difficulties that are encountered in reaching conclusions, are the facts that different human beings live and work under different conditions, and that different bodies work under different "efficiencies." To show what is meant by this term we must use machinery as an illustration. A badly cared for steam engine will require very much coal to enable it to do its work, while one that is well designed and kept in good condition will get along with much less fuel. Some human bodies are not good machines, and hence there is much loss of energy.

In this connection, the matter of digestion is of much importance. It makes little difference what the value of the food is, if its potential energy is not made use of by good digestion. As is well known, the process of digestion is dependent upon a great many factors, a few of which are the appetizing character of the food, the amount of exercise indulged in by the individual, and his nervous make-up.

It is also plain that the character of the work done by the individual will make a great deal of difference in the amount of food he requires. A professional man who sits at his desk during business hours will do far less mechanical work than a laborer who lifts heavy weights for eight or ten hours a day. The latter, we would suppose, would require considerably more food. Both ordinary observation and chemical experiments bear out this conclusion.

Experiments have also shown fairly accurate quantitative results in these matters. As a consequence, we are prepared to state with some certainty the amount of food actually required by people who live under different conditions, and who perform different kinds of work.

228. Heat Value Requirement in Foods. — If an average-sized adult man (160 lb.) did no mechanical work whatever, but sat quietly all day, he would require each day food having a heat value of from 2000 to 2100 Calories. This amount is needed merely to carry on the body processes, such as the muscular work of the heart, the movements of respiration, the work of digestion and assimilation, and keeping up the body heat. It represents the minimum amount of food. A man who does no mechanical work except that involved in going to his business, or in moving about an office or store, needs from 2700 to 3000 Calories of food value. A man doing light mechanical work, such as that a machinist or carpenter does, needs from 3000 to 3500 Calories, and a man who does heavy mechanical work such as excavating, or handling masonry or lumber material, will need from 4000 to 6000 Calories, depending upon the amount of heavy lifting that he does. Values for other conditions of life are shown in the table on page 253.

229. Protein Requirement. — In the assimilation of the large amount of carbohydrate or fat which the body needs to supply it with heat and energy, carbon and hydrogen are furnished to the organism as tissue building material in ample quantity. The supply of these two elements need not, therefore, be separately considered. But the case is different with the element nitrogen, because proteins are needed only for the purpose of furnishing this element to replace a certain amount that is excreted each day in the urine, in the form of a compound known as urea.

We get our protein chiefly from meat, but it must be remembered that many vegetables also contain this kind of food, sometimes in amounts from 8 % to 20 %. The amount of protein needed is a matter of much difference of opinion. The body has a rather remarkable power of adjusting itself to varying quantities of this kind of food, and experiments along this line have been conducted with considerable difficulty. In spite of this fact, the settlement of the question is an important matter, both because nitrogenous food is the most expensive that we buy, and because there is no reason for believing that the storage of a large quantity of protein matter, or the extra work of its elimination, is of any benefit to the organism. On the contrary, there is reason for believing that either of these conditions is disadvantageous.

The most recent experimenters have come to the conclusion that a relatively small quantity of protein is required. Where the figure was formerly put at 100 or more grams per day, one investigator has given 60 grams as an ample supply for the average individual. It would appear from all the discussion that 75 grams (about 3 ounces) is certainly enough. This is much less than most Americans eat. With such persons the excess of protein is simply used as fuel, in the place of cheaper and better carbohydrate, and the kidneys and liver have the unnecessary work of excreting unneeded nitrogen. In cases where the expense of food is a serious consideration, it is better to spend money for a sufficient amount of vegetable food to furnish the right amount of calorific value, than for an insufficient quantity of meat or other food that is rich in protein. The contrary opinion is sometimes held.

230. The Appetite as an Indication of Food Requirement. — In a healthy normal individual, the appetite is a fairly good guide to the amount of food needed. But it would be far from the truth to say that it is always a safe indicator. If the gratification of the appetite leads to the storing up of layers of excessive fat, positive harm is done, because there is interference with the healthful operation of the organism. In the same way, many people are led into the consumption of large quantities of protein material with harmful effects. On the other hand, some people, by lack of appetite, do not eat enough and their bodies are weakened. In such cases, the appetite is plainly not a safe guide. The intelligence, using known scientific facts, should be used in planning dietaries.

231. Mineral Constituents of Food. — *Iron*, although present in the body in an extremely small quantity, is of vital importance. It is contained chiefly in the hæmoglobin of the blood. When it is lacking, the individual suffers from anæmia. Spinach, lettuce, and other green vegetables are particularly rich in iron.

Chlorine is found in the body only as chlorides. We consume large quantities of sodium chloride, partly as a food and partly as a condiment. It serves many purposes in the body, and in a curious way makes us fond of vegetables rich in potassium, such as potatoes. It is said that most people eat far too much salt.

Sulphur is a constituent of most proteins, and is supplied to the body in ample and perhaps excessive amounts, in connection with this class of food.

Phosphorus. The full importance of compounds of this element as constituents of food has only lately been realized. We assimilate phosphorus from some proteins, from certain phosphorized fats, and as mineral phosphates. It has been found that there is more often a lack of phosphorus than of protein matter in food, and that some cases of malnutrition have been due to this deficiency. The desirable amount has been put as the equivalent of at least 2.75 grams of phosphorus pentoxide, P_2O_5, per day. Eggs, milk, whole-wheat bread are especially good sources of phosphorus compounds.

Calcium and *Magnesium* compounds occur as phosphates in the bones, and in the form of various other compounds in the blood and other fluids of the body. They play a very important part in the action of the heart. It is of especial importance that calcium compounds should be present in adequate amounts in the food of growing children. If lacking, arrested development and other evils may result. It has also been found that adults sometimes suffer from the lack of calcium compounds. A study of the foods of American families shows that calcium is deficient in a majority of the cases considered. The desirable amount is put as the equivalent of 1 gram of calcium oxide, CaO, per man per day.

Potassium. In spite of the chemical similarity of sodium and potassium, the two elements are not interchangeable in the body. Potassium is found chiefly in the blood as the sulphate. Here it reacts to a certain extent with sodium chloride, forming sodium sulphate and potassium chloride:

$$\underset{\substack{\text{sodium}\\\text{chloride}}}{2\,\mathrm{NaCl}} + \underset{\substack{\text{potassium}\\\text{sulphate}}}{\mathrm{K_2SO_4}} \rightleftharpoons \underset{\substack{\text{sodium}\\\text{sulphate}}}{\mathrm{Na_2SO_4}} + \underset{\substack{\text{potassium}\\\text{chloride}}}{2\,\mathrm{KCl}}$$

Both of the resulting compounds are excreted through the kidneys. Because of this action the use of common salt creates an appetite for vegetables rich in potassium.

232. Luncheons for High School Students. — As observed by chemistry teachers, these are often far from what they should be. The food selected should be nutritious, well "balanced," of moderately easy digestion, and varied in character. Where a cold lunch must be eaten (and it is not nearly so important to have hot food as it is to have well-selected food), sandwiches, or milk eaten with bread, graham crackers, or shredded wheat, make a good foundation for the meal. It is not necessary to have meat, especially when this kind of food is eaten at another time of day. The lunch should contain a considerable quantity of vegetable food, or fruits, to furnish plenty of calcium, phosphorus, and iron. It is of great importance that the appetite should not be satisfied with candy or other sweet food, since the meal would then be almost wholly lacking in protein and mineral nutrients. In the way of dessert, a little candy or other sweets may be allowed, but pies and pastry should be avoided. Cocoa or chocolate as beverages have actual food value, but this is not true of coffee, which is almost without food value, and its stimulating effect produces undesirable rather than desirable results. Milk chocolate, or milk chocolate with nuts, has high food value, but lacks some of the mineral nutrients. It is, moreover, rather concentrated in form, and should be eaten with other foods.

233. The Tables. — The data quoted in the following tables are, by permission of the publishers, taken from "The Chemistry of Food and Nutrition" by H. C. Sherman, published by the Macmillan Company.

Table I. shows the number of Calories of fuel value required at different ages. The figures given are for persons of average weight. In general the Calories required are in proportion to the weight. A woman or a girl needs as many Calories as a man or boy of the same weight, provided she is equally active.

Table II. shows the fuel value per pound of important food substances, and the per cent of protein, fat, and carbohydrate that they contain.

Table III. shows the mineral constituents (calcium, phosphorus, iron, etc.) of important foods which are rich in this class of food.

Table IV. shows the comparative economy of various foods. The difference in the cost of actual food value of common foods is seen to be astonishingly great. The prices given in the table are approximate ones. The existing prices in any community depend upon several economic factors. The average price for a year is the best for calculations.

For more complete tables see standard works, and government bulletins.

Such tables are of practical value in planning meals. It should be remembered that the appetite is an even less satisfactory indicator of the *kind* than of the quantity of food required. A person eating a very large quantity of meat would not only obtain an undesirably large amount of nitrogenous food, but also fail to obtain a proper supply of mineral substances, especially calcium and perhaps phosphorus.

TABLE I.

AGE, YEARS	WEIGHT, POUNDS	FOOD REQUIREMENT WITHOUT MUSCULAR LABOR. TOTAL CALORIES PER DAY
1	22	1000
5	37	1400
10	57	1800
15	110	2800
20	143	3000
30	152	2750
40	154	2500
60	143	2200
80	132	1600

TABLE II.

FOOD	EDIBLE PORTION			
	Protein, per cent	Fat, per cent	Carbohydrate, per cent	Fuel value, per pound, Calories.
Almonds	21.0	54.9	17.3	2940
Apples	.4	.5	14.2	285
Asparagus	1.8	.2	3.3	100
Bacon, smoked	10.5	64.8		2840
Bananas	1.3	.6	22.0	447
Beans, dried	22.5	1.8	59.6	1565
Beans, string, fresh	2.3	.3	7.4	184
Beans, baked, canned	6.9	2.5	19.6	583
Beef, corned, average	15.6	26.2		1353
Beef liver	20.4	4.5	1.7	584
Beef, roast	22.3	28.6		1576
Beef, round, lean	21.3	7.9		694
Beef, sirloin steak	18.9	18.5		1099
Beets	2.3	.1	7.4	180
Bread, graham	8.9	1.8	52.1	1189
Bread, white, homemade	9.1	1.6	53.3	1199
Bread, whole-wheat	9.7	.9	49.7	1113
Butter	1.0	85.0		3491
Cabbage	1.6	.3	5.6	143
Carrots	1.1	.4	9.3	204
Cauliflower	1.8	.5	4.7	139
Celery	1.1	.1	3.3	840
Cheese, American	28.8	35.9	.3	1990
Cheese, cottage	20.9	1.0	4.3	499
Cherries, fresh	1.0	.8	16.7	354
Chicken, broilers	21.5	2.5		493
Chocolate	12.9	48.7	30.2	2768
Cocoa	21.6	28.9	37.7	2258
Corn, green	2.8	1.2	19.0	455
Corn meal	9.2	1.9	75.4	1620
Cream	2.5	18.5	4.5	883
Dates, dried	2.1	2.8	78.4	1575
Eggs, uncooked	13.4	10.5		672
Figs, dried	4.3	.3	74.2	1437
Flour, wheat	11.4	1.0	75.1	1610
Halibut, steaks	18.6	5.2		550
Ham, smoked, lean	19.8	20.8		1209
Hominy	8.3	.6	79.0	1609

TABLE II. — *Continued*

FOOD	EDIBLE PORTION			
	Protein, per cent	Fat, per cent	Carbohydrate, per cent	Fuel value, per pound, Calories.
Lamb chops, broiled	21.7	29.9		1614
Lamb, roast	19.7	12.7		876
Lard, refined		100.0		4086
Lettuce	1.2	.3	2.9	87
Macaroni	13.4	.9	74.1	1625
Mackerel	18.7	7.1		629
Milk, skimmed	3.4	.3	5.1	167
Milk, whole	3.3	4.0	5.0	314
Muskmelons	.6		9.3	180
Mutton, leg	19.8	12.4		863
Oatmeal	16.1	7.2	67.5	1811
Olives, green	1.1	27.6	11.6	1357
Oranges	.8	.2	11.6	233
Oysters	6.2	1.2	3.7	228
Peaches, fresh	.7	.1	9.4	188
Pears	.6	.4	12.7	245
Peas, dried	24.6	1.0	62.0	1611
Peas, green	7.0	.5	16.9	454
Pie, apple	3.1	9.8	42.8	1233
Pork chops	16.6	30.1		1530
Potatoes, white, raw	2.2	.1	18.4	378
Potatoes, sweet, raw	1.8	.7	27.4	558
Prunes, dried	2.1	.	73.3	1368
Rhubarb	.6	.7	3.6	105
Rice	8.0	.3	79.0	1620
Shad, whole	18.8	9.5		727
Shredded wheat	10.5	1.4	77.9	1660
Spinach, fresh	2.1	.3	3.2	109
Squash	1.4	.5	9.0	209
Strawberries	1.0	.6	7.4	169
Sugar			100.0	1815
Tomatoes, fresh	.9	.4	3.9	104
Turkey	21.1	22.9		1320
Turnips	1.3	.2	8.1	178
Veal, hind quarter	20.7	8.3		715
Walnuts, California	18.4	64.4	13.0	3182
Watermelon	.4	.2	6.7	136
Whitefish	22.9	6.5		680

TABLE III. — IMPORTANT MINERAL CONSTITUENTS OF FOODS IN PER CENTS OF THE EDIBLE PORTION

FOOD	CaO	P_2O_5	Fe
Apples	.014	.03	.0003
Asparagus	.04	.09	.0010
Bananas	.01	.055	.0006
Beans, dried	.22	1.14	.0070
Beets	.03	.09	.0006
Blueberries	.045	.02	
Bread, white	.03	.20	.0009
Bread, whole-wheat	.04	.4	.0015
Butter	.02	.03	
Cabbage	.068	.09	.0011
Cocoa	.14	1.1	.0024
Carrots	.077	.10	.0008
Cauliflower	.17	.14	
Celery	.10	.10	.0005
Cheese	1.1	1.45	
Chocolate	.14	.90	
Corn, sweet	.008	.22	.0008
Cucumbers	.022	.08	
Dates	.10	.12	.0030
Eggs	.093	.37	.0030
Figs, dried	.299	.332	.0032
Fish, halibut	.013	.4	.0003
Grapefruit	.03	.04	.0004
Grapes	.024	.12	.0013
Lemons	.05	.02	.0006
Lettuce	.05	.09	.0010
Meat, beef, lean	.011	.50	.0038
Meat, pork, lean	.012	.45	
Meat, chicken	.015	.58	
Milk	.168	.215	.00024
Oatmeal	.13	.872	.0036
Oranges	.06	.05	.0003
Peaches	.01	.047	.0003
Pears	.021	.06	.0003
Peas, dried	.14	.91	.0056
Peas, fresh	.04	.26	.0016

TABLE III. — *Continued*

FOOD	CaO	P_2O_5	Fe
Potatoes	.016	.140	.0013
Prunes	.06	.25	.0029
Rice	.012	.203	.0009
Spinach	.09	.13	.0032
Squash	.02	.08	.0008
Strawberries	.05	.064	.0009
Tomatoes	.020	.059	.0004
Turnips	.089	.117	.0005
Walnuts	.108	.77	.0021
Wheat, entire grain	.061	.902	.0053

TABLE IV.

FOOD	PRICE PER POUND	COST OF 3000 CALORIES
Flour	$0.04	$0.08
Oatmeal	.06	.10
Sugar	.06	.10
Potatoes	.01½ (.90 per bu.)	.14
Bread	.06	.15
Beans, dried	.08	.15
Clear fat pork	.20	.16
Potatoes	.02½ (1.50 per bu.)	.24
Bacon	.25	.27
Milk	.03 (.06 qt.)	.28
Shredded wheat	.16	.28
Butter	.40	.33
Milk	.04 (.08 qt.)	.37
Olive oil	.55	.40
Milk	.05 (.10 qt.)	.46
Almonds, without shell	.60	.60
Round steak, fat eaten	.20	.88
Eggs	.24 (.35 doz.)	1.13
Round steak, fat not eaten	.20	1.26
Oysters	.15 (.30 qt.)	1.90

SUMMARY

Foods serve three purposes in the body: to act as fuel in supplying the energy necessary for muscular work; to act as fuel in keeping the body warm; and to furnish material to repair worn-out or growing parts.

The Four Classes of Foods are: fats, carbohydrates, proteins, and mineral compounds. Fats and carbohydrates are the fuels that furnish heat and energy, as well as the sources of carbon and hydrogen; proteins are needed only to furnish nitrogen for the repair of tissues; mineral compounds serve a great variety of purposes.

Food requirements may be expressed in terms (*a*) of Calories of heat available from fats and carbohydrates (proteins also furnish a certain amount of fuel value), (*b*) in grams of protein, and (*c*) in grams of mineral compounds.

An active man weighing about 160 pounds needs a total of 3000 to 3500 calories of fuel value, including the small amount that is obtained from the 75 grams of protein needed to supply nitrogen. Small, but indispensable, amounts of compounds of calcium, magnesium, potassium, sodium, phosphorus, chlorine, sulphur, and iron are also needed. Diets made up too largely of one class of foods, for example, sugar or meat, might leave the body starved for mineral constituents.

The appetite is not a safe guide to food requirement. Information concerning the composition of food and its fuel value is of great value in planning meals, especially where economy is desirable.

EXERCISES

1. What purposes does food serve in the body? From what classes of food does the body get its carbon? Its hydrogen? Its nitrogen? What other elements are needed in the body?

2. What is a Calorie? Why is the term used in expressing food values?

3. Could a person live on starch alone? Explain.

4. Which person would require more food, a tailor or a lumberman? Why?

5. Would a diet consisting altogether of meat be desirable? Explain.

6. Show, by reference to the tables, that bread may truly be regarded as the "staff of life."

7. Why should children not eat large amounts of candy? What classes of food would be lacking?

8. Why do people living in polar regions consume large amounts of fat?

9. Show the advantages of oatmeal as a food. Why should it be thoroughly cooked?

10. Compare potatoes with oatmeal as a food.

11. Show the advantages of cheese as an article of food. What are its disadvantages?

12. Calculate from the tables the lowest amount of money that you could live on for a week and meet your food requirements. Consider your age, weight, and degree of activity.

13. Show why milk chocolate, or chocolate with nuts, makes a good extra food for strenuous exertion like mountain climbing.

14. What mineral compounds are apt to be lacking in American diets?

15. What purposes do such foods as lettuce and spinach serve?

16. Using the tables, plan three simple, appetizing meals that would meet the food requirements for a day, of a family of five adults, all moderately active people. Give the weights of the various foods that you would use.

17. Plan three vegetarian meals that would meet your own food requirements for a day. Give the weights of the food.

CHAPTER XXII

THE COOKING AND THE ADULTERATION OF FOODS

234. The Cooking of Foods. — In the preparation of food, cooking serves several purposes. The main purpose, except in the case of substances containing starch, is to secure variety of flavor, or to improve the flavor. This is a matter of dietic importance, since appetizing quality hastens digestion. Hence the art of cooking is an important one, and the cook does well to impart a fine flavor to her preparations. In the case of starchy foods, greater ease of digestion is secured by cooking, for the reason that the starch granules are burst open and the starch is more directly accessible to the action of the digestive fluids. But most other foods are as easily, or more easily, digested in the raw state. The cooking process, as a rule, does not materially affect the food value. Cooking serves a very important hygienic purpose by killing any disease germs that may exist in the raw food.

235. The Cooking of Meats. — The most important thing to bear in mind in the cooking of meats is that protein matter is *coagulated* (made tougher, firmer) by the application of heat. Gelatinous matter is also melted or dissolved by the action of the heat and by the action of the juices that are produced. The principal methods of cooking meat are: broiling, baking, stewing, and frying; roasting on a spit is infrequently used in this country.

Broiling is the best method of cooking small cuts of meat, such as steaks and chops. They are exposed to the direct, intense heat of coals or hot iron plates of the gas stove, and the process is completed in a short time. The high temperature coagulates the albumen of the surface immediately, and the juices which are produced during the cooking of the inner portions cannot easily escape. These juices are highly flavored and contain the mineral constituents. A properly cooked steak or chop presents a "puffed" appearance due to the expanding action of the steam that cannot easily escape through the surface membrane of coagulated albumen. An old saying, "In cooking meat, the larger the cut the lower the temperature," is a good one; of course, this also implies that the process is longer with the larger cut. Hence whole poultry and roasts are subjected to the process of so-called roasting, which is, however, really *baking.* The lower temperature is necessary because otherwise the outer layer would be charred before the inner parts were heated to the cooking temperature (about 180° F.). The roast should be put into a *hot* oven to accomplish the coagulation of the outer layer, as in broiling; the process should then be continued at a lower temperature. As the cooking proceeds, a considerable quantity of meat juice collects in the baking pan, and the roast tends to become dry and to lose much of its flavor. To counteract this tendency, the juice should be dipped up from time to time and poured over the meat, a process called *basting.*

Stewing consists of cooking food in hot water. Practically, the temperature cannot go above the boiling point (212° F.), and, in the case of meats, this temperature is not desirable, except for a few minutes at the beginning of the operation. A temperature of about 180° is preferable. If the purpose is to make a soup, or a "stew," in which the broth is consumed as part of the dish, the cooking should begin in cold water, since in this case it is desired to extract the flavor and nutriment of the meat as much as possible.

Frying, if properly done, is the stewing of food in fat or grease. It is not a very desirable way of preparing meat, because the protein matter is too much coagulated by the high temperature of the heated fat, which can become much hotter than boiling water. This may not happen if the process is completed very quickly. A certain amount of indigestible fat also clings to the food.

Roasting, properly speaking, means the cooking of large cuts of meat before an open fire on a spit. Chemically considered, the process resembles broiling very closely, except that the meat is not exposed to so high a temperature. Both roasting and broiling may be described as "the stewing of meats in their own juices."

236. Digestion of Foods.—Digestion takes place by means of both physical and chemical changes. The physical processes consist in the chewing of the food and the involuntary movements of the walls of the stomach and the intestines. These processes result in a thorough mixing of the food with digestive fluids, which are secreted by different organs of the body and introduced into the digestive tract at intervals. A further effect of the physical processes is the thorough breaking up of the food particles, until finally they are in a practically liquid state. An important part of this work is the "emulsifying" of fats; this means that they are broken up into such small globules that they mix with water to form a liquid of uniform composition that will not separate into layers. In this form the fats can be directly absorbed.

The chemical changes of the digestive process are accomplished largely under the influence of a class of substances called *enzymes.* These are complicated organic compounds which act as catalytic agents, since they produce chemical changes in amounts of food relatively very large in comparison to their own quantity. Such catalytic agents are very numerous in the body ; they are found in the saliva, in the gastric, intestinal, and pancreatic juices, and in the blood and muscular tissues. It is the office of these numerous enzymes to prepare food for direct absorption by the blood and all the many tissues of the body. They do so by breaking up complex molecules into simpler ones by the process of hydrolysis. As a few examples of the work they accomplish, we may mention:

(*a*) the conversion of starch into maltose;
(*b*) the conversion of maltose into glucose;
(*c*) the splitting and oxidation of glucose;
(*d*) the splitting of fats into fatty acids and glycerin;
(*e*) the splitting of proteins into proteons, peptones, etc.

237. Adulteration in Foods. — *Preservatives* are frequently used in foods. We may divide them into two classes: those which are of the nature of condiments or flavors and those which have no effect on the flavor. The use of the first class, preservatives like salt, sugar, vinegar, spices, smoke (in meats), is generally regarded as permissible, especially since they have a real, immediate value in stimulating digestion through their pleasant flavor. As examples of the second class, whose use is generally held to be undesirable, we have boric acid, benzoic acid, benzoate of soda, formaldehyde, sulphur dioxide, and salicylic acid. The presence of any of these substances is easily recognized by simple tests.

Artificial coloring is used to give food an attractive appearance. Various dyes, copper salts, turmeric, and caramel (burnt sugar) are the substances most used for this purpose. Many of these are actually injurious, and in general no adequate reason exists for the use of artificial coloring of any kind. The public, by giving altogether too much attention to *appearance* in buying food, is largely responsible for this kind of adulteration.

Adulteration and substitution. Under this head, we may mention as substitutes for olive oil the use of cottonseed oil and peanut oil, either alone or mixed with olive oil or with lard; glucose in place of sugar products; saccharine as a sweetener; starch in jellies and spices; chicory and cereals in ground coffee. Flavoring extracts, such as lemon and vanilla, are often subject to adulteration with cheaper extracts of similar flavor, or with artificially made essential oils. In this country vinegar made from cider is supposed to be the standard, but it may be made from alcohol and water, from malt or wine, and improperly sold as cider vinegar. Flour is bleached by treatment with nitrogen peroxide in order to make it very white.

These adulterations are objectionable in two ways. Food of this sort may be harmful when eaten, and it is certainly a fraud. Articles that are sold below a reasonable cost of production should be viewed with great suspicion.

238. Canned Goods. — These are generally good in quality in this country. If the inside of the can appears to have been acted on by the contents, metallic salts, tin, and possibly lead may be present. Meat and fish bought in cans should be examined very carefully for any signs of putrefaction, which is especially dangerous in this kind of food. If gas issues from the can when it is punctured, or if there is any other sign of putrefaction, the contents should be thrown away. Even cooking does not counteract the *ptomaine* poisons that may be present.

SUMMARY

Cooking improves the flavor of foods, kills the disease germs that may be present, and, in the case of foods containing starch, increases the digestibility.

In cooking meats, whether by broiling, baking, or roasting on a spit, the flavor is better if the outside layer of the meat is coagulated as quickly as possible by high temperature at the beginning of the operation. Large cuts of meat should be cooked at a lower temperature than small cuts. Meats are best cooked at a temperature of about 180° F. after the initial coagulation.

Frying is not an altogether desirable way of cooking food.

Starch is made more digestible by cooking, because the cells of which it is composed are burst open by the heat, and the molecules are more directly subject to the action of digestive fluids.

Digestion takes place by both physical and chemical changes. The physical processes result in the breaking up of the food into small particles. The chemical processes are catalytic actions induced by enzymes that split up the food molecules by hydrolysis into simpler substances. The presence of water is essential to these operations.

Adulterants are used in foods (*a*) to preserve them from fermentation or decay, (*b*) to make them more attractive in appearance, or (*c*) to substitute a cheaper for an expensive article.

Preservatives commonly used are: benzoate of soda, benzoic acid, salicylic acid, boric acid, formaldehyde, sulphur dioxide. Preservatives such as salt, sugar, vinegar, or spices are not usually classed as adulterants.

Colorings. Canned vegetables, canned fruits, and beverages are sometimes colored with organic dyes, copper salts, or caramel. Flour is bleached by nitrogen peroxide.

Substitutions. Starch, saccharine, and glucose are substituted for cane sugar in preserves and jellies. Olive oil is adulterated with other vegetable oils.

EXERCISES

1. Why does cooking make starchy foods easier of digestion?

2. Why should oatmeal be cooked very long and thoroughly?

3. Why are most foods cooked before being eaten?

4. What is the effect of heat on protein foods? Does this affect the digestibility in any way?

5. Show how, by a kind of process of survival, the race has come to have a taste for cooked food.

6. In roasting or broiling meats, why is it desirable to begin the operation at a high temperature?

7. What is a proper temperature for finishing the roasting of meats? Why?

8. Distinguish between the broiling, baking, and roasting of meats. Why is broiling better than frying as a means of cooking steaks and chops?

9. In making a soup from meat, should the meat be put into hot or into cold water? Why? Should the time be long or short?

10. Why should food be thoroughly chewed before it is swallowed?

11. What happens to food in the process of digestion?

12. Name some common kinds of food adulteration.

13. What precautions should be taken in using canned fruits and vegetables? In using canned meats?

14. Why should manufacturers be required to date all canned goods?

15. Name some adulterations that result from the effort to give food an attractive appearance.

16. Oleomargarine has good food value. What objection is there to its sale as butter?

CHAPTER XXIII

BREAD MAKING

239. Bread as a Food. — Bread is so important a part of human food that the term is often used figuratively to stand for all food, as in the phrase "Man shall not live by bread alone." If we were to define the term we should say that bread means a form of food made from the flour of some grain, as wheat or rye, in such a way that it has more or less porous structure. This porosity is essential to easy digestion, and it has meant much to the race that long ago a way was discovered of giving bread this quality.

240. Wheat Flour. — Most of the bread used in this country is made from wheat flour. This is obtained by crushing the wheat kernel between steel rollers and sifting the product to remove particles of husk. The finely divided substance thus obtained is composed of starch and gluten, together with small quantities of sugar and dextrin. Starch is a definite chemical compound whose composition may be represented by the formula $(C_6H_{10}O_5)_n$. It belongs to a class of substances known as *carbohydrates*, and is useful as food because it is oxidized in the body processes, and thus furnishes heat to the organism. Gluten, on the other hand, is valuable because it contains nitrogen compounds which are needed to build up muscle tissues. Wheat makes the best of grain foods because it contains the highest proportion of gluten.

241. Importance of Porous Structure in Bread. — Owing to the high proportion of gluten, wheat flour has a very adhesive quality when mixed with water. If very little water is used we get a tough, tenacious mass which we call dough. It is quite apparent that such a substance would be difficult to digest, if we remember that the process of digestion is carried on by the chemical action of fluids, such as saliva and gastric juice, which are secreted in the body. They could not permeate a non-porous dough, and, moreover, both starch and gluten are rather hard to digest. Hence all breadstuffs are made porous or "light" by some device or other. When such food is eaten, the digestive fluids penetrate it easily, as water enters a sponge, and every particle of the food is subjected quickly to their digestive action.

242. Use of Yeast in making Bread Light. — The use of yeast for giving a porous structure to bread is an ancient method that has never been improved upon for making digestible bread of excellent quality. Yeast is a microscopic plant (Fig. 77) which grows or multiplies in solutions of sugar, provided nitrogen compounds and certain salts are also present. In its growth it secretes ferments which act catalytically on the sugars present in the flour, causing a fermentation that yields carbon dioxide and alcohol. The amount of sugar that is subjected to this action is increased by the fact that flour contains diastase, a ferment which changes part of the starch into a sugar:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{alcohol}}{2\,C_2H_5OH} + \underset{\text{carbon dioxide}}{2\,CO_2}$$

When yeast is put into dough, and the mixture is put in a warm place, the yeast grows and carbon dioxide is produced. The gas permeates the dough, but cannot escape because of the tenacious character of the mass. As a result, the dough "rises," that is, it swells up because of the bubbles of gas that have been formed within it.

The reason that wheat flour makes the best bread is that the dough which it gives is especially tenacious because of the high proportion of gluten. Rye stands next to wheat in this respect. Flour from some grains will not make bread at all, because it does not contain enough gluten to make a plastic, tenacious dough.

FIG. 82.—DOUGH AFTER KNEADING.

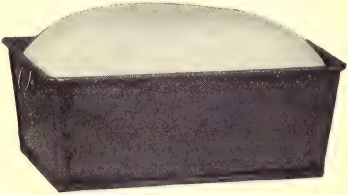


FIG. 83.—LOAF AFTER "RISING."

243. Kneading the Dough. — After the dough has risen, the baker rolls and folds it, and by this process breaks up the irregularly sized bubbles of gas, and distributes them evenly through the mixture. He then shapes the dough into loaves, and sets them to rise again (Fig. 82). The fermentation continues to go on because the yeast is still growing and secreting ferments in the mixture of flour and water. More carbon dioxide is produced and makes the dough rise in the pan (Fig. 83).

244. Baking the Bread. — The raised loaves are next put into a hot oven to bake. The first action of the heat is to expand the bubbles of carbon dioxide, and the loaf is made very porous or light (Fig. 84). The yeast is killed, fermentation stops, and at the same time the alcohol and part of the water are vaporized and driven off. Starch as it exists in flour has an organized, cellular structure, in which form it is not easily digestible. In baking, these cells are exploded by the heat and the starch is made more easily subject to the action of the digestive juices. The outside of the loaf becomes very hot, and chemical changes take place there which do not occur on the inside because this never gets hotter than the boiling point of water, 100° C. This is due to the fact that during the entire process of baking, water is being continually turned into steam inside the loaf. In the outside crust, because of the greater heat, starch has been largely converted into dextrin, another carbohydrate, and this in turn is partly converted into caramel. For this reason the crust of bread has an entirely different taste from the interior of the loaf.

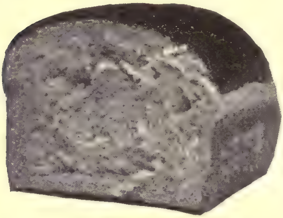


FIG. 84.

245. Other Means of making Bread Porous. — A number of other methods have been tried for making porous bread. One of these consists in mixing the dough in a gas-tight vessel into which carbon dioxide is introduced under considerable pressure. The mixture is stirred in the vessel until the compressed carbon dioxide is mingled with the dough. The charged dough is then allowed to escape from the bottom of the vessel. As it issues, the diminished pressure allows the gas to expand, and the dough, which has meanwhile been cut into loaves, "rises." The baking proceeds as with other bread. Made in this way, however, bread is not so tasty or digestible as yeast-made bread.

Another method consists in mixing a small quantity of sodium bicarbonate with the flour, and in using a small quantity of dilute hydrochloric acid in mixing the dough. As the acid and bicarbonate come together, they react, forming common salt and carbon dioxide.

$$\underset{\substack{\text{sodium}\\\text{bicarbonate}}}{NaHCO_3} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{HCl} \longrightarrow \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2} + \underset{\substack{\text{sodium}\\\text{chloride}}}{NaCl} + \underset{\text{water}}{H_2O}$$

This method closely resembles the use of baking powder.

246. Adulterants in Bread Making. — The addition of a small amount of alum to dough makes bread of exceptionally fine appearance. This is due to the fact that alum increases the plastic quality which gluten gives to the mixture of flour and water. It does no real good, and perhaps impairs the digestibility of the bread. Copper sulphate is used for the same purpose and is even more objectionable. Limewater is said to improve the appearance of the loaf in a similar way, and its use would do no harm.

247. Salt-rising Bread. — In some parts of the country it is the practice of housewives to make a kind of bread whose taste is quite different from that of ordinary bread. The process differs from that employed for yeast bread only in the means used for bringing about the fermentation. Corn meal and a little soda and salt are mixed with hot water or milk. After some hours, this batter, called "emptyings," starts to ferment and carbon dioxide is produced. Dough is made as for ordinary bread, and the "emptyings" are added in the place of yeast. The fermentation continues, and the loaf becomes porous from the production of carbon dioxide.

This method is especially interesting because it has recently been the subject of a scientific investigation. As a result, salt-rising bread can now be made in bakeries on a large scale, with scientific certainty of result, whereas formerly efforts to do this had been unsuccessful, for the reason that the organism causing the fermentation was not known, and the conditions favorable for its growth were not understood. The investigator discovered the bacterium that is responsible for the production of the gas, and found that it gets into the mixture from the corn meal, with which it seems to be always associated. It grows best when milk is also present, owing to the fact that this substance contains casein. This experience indicates that we may expect greatly improved knowledge of cookery from the application of scientific method to its study.

248. Leavened or "Raised Foods" other than Bread. — So far we have been speaking of bread in the common meaning of the term. In reality, however, such things as cake, biscuits, and muffins are of the same nature as bread, since they consist mostly of flour, and are made porous in the process of cooking. Some device other than yeast is generally employed in order to save time.

249. Baking Powders. — The most important of other leavening agents is the combination of dry, powdered substances that will react chemically in the presence of moisture to produce carbon dioxide. Such mixtures are called baking powders. They all contain sodium bicarbonate, $NaHCO_3$. This is the substance from which the carbon dioxide comes. The other constituent is of such a nature that it will act as an acid in the presence of moisture. The principal materials so used are:

First, potassium acid tartrate (cream of tartar), $KH(C_4H_4O_6)$; its molecule contains one *acid* hydrogen atom, and the action with sodium bicarbonate is:

$$\underset{\substack{\text{sodium}\\\text{bicarbonate}}}{NaHCO_3} + \underset{\substack{\text{acid potassium}\\\text{tartrate}}}{KH(C_4H_4O_6)} \longrightarrow \underset{\substack{\text{sodium potassium}\\\text{tartrate}}}{KNa(C_4H_4O_6)} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

Second, monocalcium phosphate, $CaH_4(PO_4)_2$; its action is:

$$\underset{\substack{\text{sodium}\\ \text{bicarbonate}}}{2\,NaHCO_3} + \underset{\substack{\text{monocalcium}\\ \text{phosphate}}}{CaH_4(PO_4)_2} \longrightarrow$$

$$\underset{\substack{\text{calcium hydrogen}\\ \text{phosphate}}}{CaHPO_4} + \underset{\substack{\text{disodium}\\ \text{phosphate}}}{Na_2HPO_4} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{2\,CO_2} + \underset{\text{water}}{2\,H_2O}$$

Third, alum, $KAl(SO_4)_2$, or sodium aluminum sulphate, $NaAl(SO_4)_2$; these substances contain no acid hydrogen, but when dissolved in water, they produce a very small quantity of sulphuric acid,

$$\underset{\text{alum}}{2\,KAl(SO_4)_2} + \underset{\text{water}}{6\,H_2O} \longrightarrow \underset{\substack{\text{sulphuric}\\ \text{acid}}}{3\,H_2SO_4} + \underset{\substack{\text{potassium}\\ \text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{aluminum}\\ \text{hydroxide}}}{2Al(OH)_3}$$

The result when acting with sodium bicarbonate is,

$$\underset{\substack{\text{sodium}\\ \text{bicarbonate}}}{6\,NaHCO_3} + \underset{\text{alum}}{2\,KAl(SO_4)_2} \longrightarrow$$

$$\underset{\substack{\text{aluminum}\\ \text{hydroxide}}}{2\,Al(OH)_3} + \underset{\substack{\text{potassium}\\ \text{sulphate}}}{K_2SO_4} + \underset{\substack{\text{sodium}\\ \text{sulphate}}}{3\,Na_2SO_4} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{6\,CO_2}$$

250. Healthfulness of Baking Powders. — As will be seen from the above equations, one or more products of chemical reaction remain in the food after baking. Besides these products, one of the constituents of the original powder will also remain, if the ingredients of the powder were not mixed in the exact proportion for complete chemical action. The possibly harmful action of these substances has been the subject for considerable discussion. Unfortunately, there is not much reliable experimental observation on which to base conclusions. The investigations that have been carried on have been for the most part at the expense of some manufacturing firm that was financially interested in the result. Consequently there has not been that freedom from bias which is desirable in scientific work.

More has been said against alum (or sodium aluminum sulphate, $NaAl(SO_4)_2$, which chemically closely resembles alum) than any of the substances named above as constituents of baking powders. Nevertheless this substance is said to be present in a majority of the powders that are on the market. Chemists agree in thinking that alum itself would be very undesirable in food; but in making baking powder, care is supposed to be used so that the alum is mixed with bicarbonate in such proportion that the two will exactly "balance" during the baking process. If this happens, the products left in the food are aluminum hydroxide, sodium sulphate, and potassium sulphate. Opinion is not altogether agreed that these have a harmful effect. Since alum powders are so largely used, it is apparent that no easily discernible evil effect follows their use.

Starch or flour is usually added to the baking powder mixture. Besides increasing the bulk, this serves to dilute the powder and thus assists in keeping it from deteriorating.

Ammonium bicarbonate is sometimes used in baking powders. It helps to make the dough light because on being heated it decomposes into gaseous products:

$$\underset{\substack{\text{ammonium}\\\text{bicarbonate}}}{NH_4HCO_3} \longrightarrow \underset{\text{ammonia}}{NH_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

Tests for alum and ammonium compounds in baking powders are very easily made.

251. Sour Milk and Soda for Leavening Agents. — Milk contains a sugar known as lactose, $C_{12}H_{22}O_{12} \cdot H_2O$. When souring occurs, this substance is transformed by fermentation into lactic acid, $HC_3H_5O_3$:

$$\underset{\text{milk sugar}}{C_{12}H_{22}O_{11}.H_2O} \longrightarrow \underset{\text{glucose}}{2\,C_6H_{12}O_6};$$

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{lactic acid}}{2\,HC_3H_5O_3}$$

The lactic acid thus produced in sour milk will react with soda (sodium bicarbonate) and produce carbon dioxide. This method is much employed in the household as a quick means of making muffins or griddle cakes light.

$$\underset{\text{soda}}{NaHCO_3} + \underset{\text{lactic acid}}{HC_3H_5O_3} \longrightarrow \underset{\text{sodium lactate}}{NaC_3H_5O_3} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

The residue of the milk, consisting mostly of casein and albumen, remains in the food and adds value to it. The flavor that it incidentally gives is a further reason for using this means of leavening.

252. Pastry. — Pie crust and similar forms of pastry are not leavened, properly speaking. Instead, the flour is so treated that when baked it readily crumbles into thin flakes, and the desired effect of exposing much surface to the action of digestive fluids is thus obtained. By the housewife, this method is termed "shortening." Fat in the form of lard, butter, or oil is mixed with flour and water, and the dough thus obtained is rolled into a thin layer. This is folded on itself, rolled again, and the process repeated many times. In this way, air is caught and retained between the layers, and expanding under the heat of the oven, it plays an important part in producing a flaky crust. Shortening is used in making many forms of cake, and in biscuits and crackers.

SUMMARY

Flour is made by grinding kernels of grain to a powder and sifting out the husk. The chief food elements are starch, gluten, and a small quantity of sugar.

To make flour easily digestible it is necessary to (*a*) cook it in some manner in order to break up the starch cells, and (*b*) to make the finished product porous or "light."

Wheat Flour is better for bread making than that from other grains because it has a higher per cent of gluten; this substance is necessary to make the dough coherent and plastic.

The chief means of making cake and bread light are (*a*) yeast, and (*b*) baking powders. Both produce small bubbles of carbon dioxide gas within the dough. During the baking these expand and produce the desired porous character.

Yeast is a microscopic organism which, during its growth, secretes ferments that convert sugar into carbon dioxide and alcohol.

Baking Powders consist of sodium bicarbonate mixed with some solid acid, or acid-forming substance, in powder form. Cream of tartar (potassium acid tartrate), calcium acid phosphate, or alum is most commonly used as the acid constituent.

Sour Milk contains lactic acid and is used with sodium bicarbonate (soda) to make some kinds of food light.

Salt-rising Bread is raised by an organism that acts somewhat as yeast does.

"**Shortening,**" that is, butter or other fat, makes food flaky rather than light, but serves a similar purpose in putting the food in such condition that much surface is exposed to the action of digestive fluids.

EXERCISES

1. Why is it desirable to have bread, cake, and other flour foods made light, though this is not true of other forms of food?

2. Why will not rice flour make a good bread? What other grains besides wheat will serve for bread making?

3. Why is thorough cooking necessary when oatmeal is used as a breakfast food?

4. How is easy digestibility secured in such foods as macaroni, spaghetti, etc.?

5. What is yeast? What is meant by the statement that it acts *indirectly* in producing carbon dioxide? Write an equation for the reaction that produces the carbon dioxide.

6. What undesirable quality has bread that has not been allowed to "rise" sufficiently? That which has been allowed to "rise" too long? Why?

7. Why does the action of yeast stop after the bread has been baked?

8. What is baking powder?

9. Compare yeast and baking powder as leavening agents. Why is yeast nearly always used in bread making, and baking powder in cake making?

10. Explain how alum acts as an acid in water solution.

11. Give the formulas of baking soda, cream of tartar, glucose, alcohol, and starch.

12. Write an equation to show how carbon dioxide is produced by the action of baking powder.

13. Why should baking powder be kept in a tightly closed tin can?

14. Why should the baking powder be mixed with the flour before any liquid is added?

CHAPTER XXIV

MILK

253. Necessity for Purity. — No article is more frequently used for food than milk, and there exists no food concerning the production and handling of which greater care should be exercised. Since milk is one of the few foods consumed uncooked, any disease germs that it contains are likely to be in an active condition when the milk enters the stomach. In our large cities, the death rate of children under five years of age has been repeatedly shown to bear a direct relation to the quality of milk furnished in the open market.

254. Composition. — The essential constituents of milk are water, milk sugar, protein, and salts (chiefly phosphates and chlorides). While these substances are found in the milk of all mammals, the percentage composition of milk varies greatly with the kind of animal producing it. The composition varies to a less degree among animals of the same species and to a still more limited degree at different times in the case of the same animal. The general percentage composition of the milk of four species of mammals has been given as follows:

	Cow	Goat	Horse	Human
Water	87.17	85.70	90.75	87.41
Sugar	4.88	4.44	5.70	6.21
Fat	3.69	4.75	1.20	3.78
Protein	3.55	4.30	2.00	2.29
Ash	0.71	0.80	0.35	0.31

255. Cow's Milk. — The word milk, when unqualified, means the milk of the cow, which is practically the only kind of milk that is an article of commerce. The Board of Health of New York City has ruled that milk containing more than 88.5% of water, or less than 3% of fat, or less than 11.5% of solids, cannot be legally offered for sale in the city. While many cases have been known in which the milk of an individual cow has contained more water or less fat and total solids than required by the Board of Health, such a milk would be considered of too low a grade for human consumption.

256. Source and Handling of Milk. — The source of milk demands most careful attention. Milk drawn from an unhealthy cow is unfit for use as food. There is little doubt that the drinking of milk from tuberculous cows has been a frequent cause of tuberculosis in human beings. A careful examination of the physical condition of the cow producing the milk is, however, no more essential than the prevention of disease germs entering the milk after it has been drawn from the cow. Typhoid fever, scarlet fever, and diphtheria have been repeatedly caused by persons drinking milk containing the germs of these diseases. Dangerous germs fall into the milk at milking time from the uncleaned surface of the cow or from the hands and clothing of a milkman who himself has, or has been exposed to, some contagious disease. Germs may enter the milk with the dust from hay or straw stored on a loose floor above the cow stall. Disease germs may also enter the milk from the vessel into which it is drawn, or in which it is stored, if the vessel is washed with contaminated water or if, after use, it is not sterilized by boiling water or by steam. Dangerous germs are carried by the wind and by insects; therefore, milk utensils should be protected from these agencies. The milk supply of a large city has to be transported over long distances, so that little of it reaches the consumer in less than 24 hours after production, and much of it must be kept sweet from 2 to 4 days. Milk is an excellent medium in which to grow bacteria. If it becomes infected soon after production, there is time for the bacteria to increase to inconceivable numbers before the milk is used. At 38° C. or 100° F. one bacterium will increase to 75,000 in 24 hours; at 21° C. or 70° F. one bacterium will increase to 760 in 24 hours; below 10° C. or 50° F. the bacteria in milk will increase very slowly. The Boston Board of Health prohibits the sale of milk which contains more than 500,000 bacteria per cubic centimeter, or which is delivered at a temperature of more than 50° F.

257. Souring of Milk. — The changes that take place in milk on standing are chiefly due to low forms of life which multiply with enormous rapidity in milk. The most noticeable change that takes place is the souring of the milk. This is owing to forms of bacteria, known as the lactic acid bacteria, that enter the milk and rapidly multiply in it. They convert the milk sugar, which is sweet, into lactic acid, which is sour. The lactic acid soon accumulates to a quantity sufficient to cause one of the proteins, casein, to separate, leaving behind a thin liquid called *whey*. In other words, the lactic acid causes the milk to curdle.

258. Putrefaction of Milk. — At the same time the lactic acid fermentation is going on in the milk, putrefactive bacteria are at work. While at first they work less rapidly than the lactic acid bacteria, they soon cause some of the casein to decompose, thus producing poisonous substances, ptomaine poisons. Such milk is absolutely unfit for food.

The putrefactive bacteria are less easily killed by heat than the lactic acid bacteria.

259. Methods of Keeping Milk Sweet. — Since the forms of bacteria that cause milk to sour are present in large numbers in the air, it is not possible to keep sweet for more than a day or two pure milk that is exposed to the air at ordinary temperature. In order to have pure milk remain sweet for several days, the utmost care must be taken to protect it from dust and from filth of every description and, moreover, it must be kept at a temperature little above the freezing point, so that the bacteria which unavoidably enter the milk will multiply very slowly. All this adds greatly to the expense of handling the milk and puts the price beyond what the average citizen can afford to pay.

Two methods that do not add materially to the selling price have been extensively employed to increase the time milk will keep sweet. One of these is to add some chemical as a preservative, and the other is pasteurization.

260. Preservatives. — The preservatives that have been most extensively employed in milk are formaldehyde, boric acid, and borax. These are objectionable on account of their poisonous properties. Although they are generally added to milk in very small quantities, especially in the case of formaldehyde, they should never be used. Particular care should be exercised to see that they are kept out of milk for infants. Sodium bicarbonate has recently come into use as a preservative.

261. Pasteurized Milk. — True pasteurization of milk consists in heating it to a temperature of from 145° F. (63° C.) to 167° F. (75° C.), keeping the milk from 20 to 40 minutes between the temperatures mentioned, then rapidly cooling the milk and keeping it at a low temperature until delivered to the consumer. Milk that has been held at the temperature mentioned for less than a minute has so frequently been sold as pasteurized that Boards of Health are beginning to demand that the milk, after being raised to the required temperature in the pasteurizing machine, shall be run into a holding machine. One form of holding machine is made up of compartments which revolve slowly and are so arranged that milk entering one compartment is kept at a temperature of at least 140° F. for 20 minutes before it can be delivered to the cooling apparatus

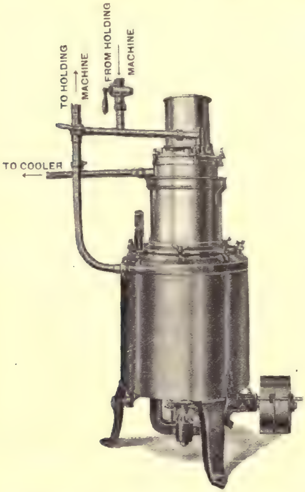


Fig. 85. — Willmann Regenerative Pasteurizer.

Milk that has been improperly pasteurized may keep sweet for a considerable period of time and yet be then more dangerous to use than raw milk. The lactic acid bacteria are quite readily killed by a short exposure to a temperature of 160° F., while spore-bearing putrefactive bacteria are little affected. The customer, depending on the sweetness of the milk as an indication of its purity, fails to realize that it may contain putrefactive bacteria and the poisons produced by them.

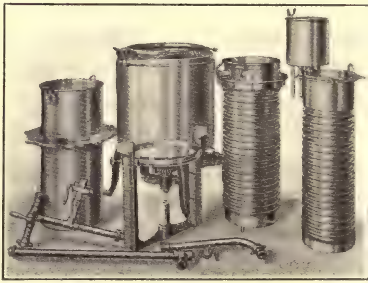


Fig. 86. — Willmann Regenerative Pasteurizer taken Apart.

The consumer should realize that at best pasteurized milk is not sterilized milk. Since it is not entirely free from undesirable germs, it should be kept at as low a temperature as is necessary for preventing the rapid growth of bacteria, or better still, it should be consumed within a few hours after pasteurization.

It is fortunate that the disease-producing germs generally found in milk are not spore-bearing and are killed by the temperature used in pasteurization. There is no doubt that a milk carefully pasteurized and kept cool until needed, is far safer than ordinary raw milk.

262. Certified Milk. — Milk commissions have been formed in various parts of the country to formulate and enforce rules governing the production and handling of a portion of the milk to be placed on the market. Milk dealers have a right to label their milk as being certified by a milk commission when the commission grants them that privilege. This is done only after a thorough inspection has been made of the herd of cows producing the milk, of the water supply of the dairies, and of all utensils used in handling the milk. The rigid enforcement of the rules governing the production and handling of certified milk insures to the purchaser a clean, pure milk from a healthy cow. A certified milk is likely to be of unimpeachable quality only when the milk commission is composed of upright, energetic men who are untiring in their efforts to have the rules of the commission enforced. It should be remembered, however, that it is the method of production and not the milk that is certified.

263. Modified Milk. — If an infant is to be fed on cow's milk, it is essential not only to have the milk pure and sweet but, in addition, its composition should be changed so as to have it resemble mother's milk as closely as possible.

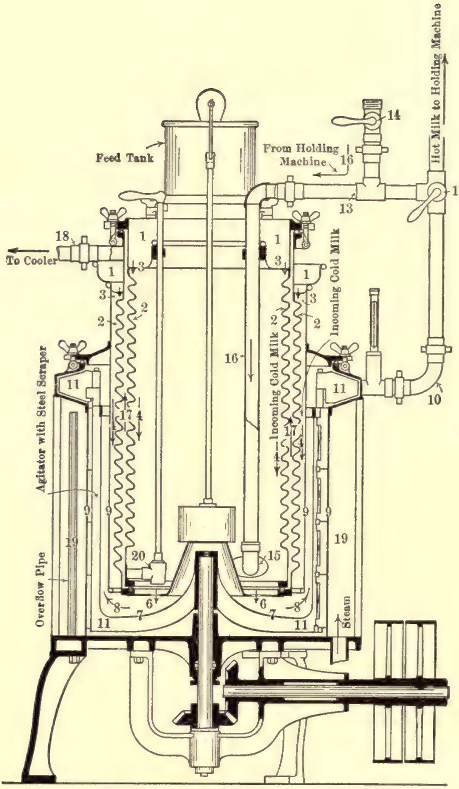

Hot Milk to Holding Machine
14
Feed Tank
From Holding Machine
16
12
13
18
To Cooler
1
1
1
1
3
3
3
3
Incoming Cold Milk
2
2
2
2
16
Incoming Cold Milk
Agitator with Steel Scraper
11
11
10
17
4
17
4
4
4
9
9
9
9
19
19
20
15
Overflow Pipe
8
6
7
6
7
8
11
11
Steam

FIG. 87. — REGENERATIVE PASTEURIZER, SECTION THROUGH AXIS.

The cold milk is led into the feed tank of the Willmann pasteurizer (Fig. 87) from which it is equally distributed into the troughs 1-1, whence it is distributed over the corrugated surfaces 2-2-2-2, through small perforations, as indicated by the arrows 3-3-3-3, and flows by gravity over the corrugated surfaces as indicated by the arrows 4-4-4-4 until it reaches the bottom of the corrugated section, when it passes through the openings, indicated by the arrows 6-6, into the space 7-7. Its course is then turned upwards, as shown by the arrows 8-8, into the space between the plates 9-9-9-9, where the temperature is raised to 145° F., and the milk is thrown out into the pipe 10 by the revolving agitator 11-11-11-11. From this pipe 10 the milk is led into the holding machine. The valve 12 is a 3-way valve which can be turned so that the milk will be carried to the holding machine, or into the pipe 13 Pipe 13 is used when no holding machine is employed and when the machine is first started, until the temperature of the first milk is raised to 145° F. The hot milk from the holding machine is brought back through the valve 14 to the pipe 13 which leads to the bottom of the corrugated section and connects to the space between the corrugated sections at 15. The hot milk flows as shown by the arrows 16-16

Before such a change can be made intelligently, it is necessary that the composition of the milk to be modified should be determined, that is, the milk must be analyzed. This should be done only by a trained milk chemist.

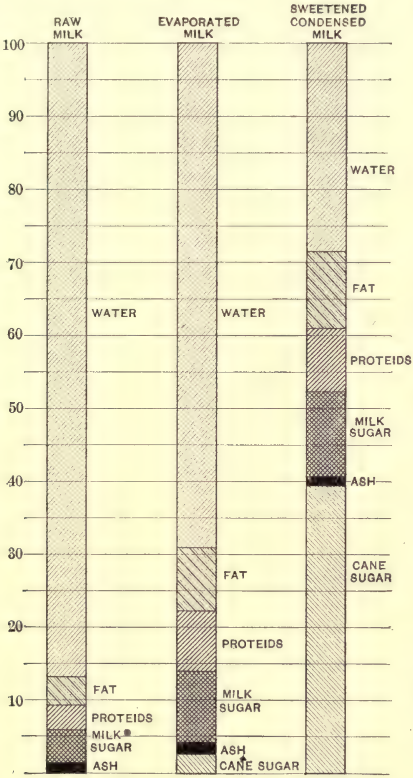


FIG. 88. — PERCENTAGE COMPOSITION OF MILK.

264. Sterilized Milk contains no living organisms. The killing of the germs in the raw milk removes the danger that might arise from taking into the system disease-producing bacteria. Sterilization is generally accomplished by boiling the milk. This will not kill the spores of bacteria, and hence the milk must be allowed to cool so that any spores which it contains may start to grow. Then it should be heated again.

265. Evaporated Milk is milk that has been concentrated until it contains not less than 28% of milk solids of which 7.7% is milk fat. It is unsweetened and is sold in sealed

through 15 and then upward between the corrugations, as indicated by the arrows 17-17, and out through the pipe 18. The hot milk is thus cooled and the cold milk heated. Valve 20 is for driving the hot milk from the space between the corrugations.

The final heating is accomplished by hot water in the space 19-19 against the surfaces 9-9, and the final cooling by a cooler separate from the pasteurizer.

cans. In the production of any form of condensed milk, the greatest care has to be exercised to obtain a high quality of raw milk, if an attractive article is to be manufactured. The evaporation is carried on in vacuum pans so that the milk is not heated to a sufficiently high degree to impart to it a cooked flavor. It is then commonly put through a homogenizer (§ 269) to prevent the separation of fat. After being sealed in cans, the evaporated milk is sterilized by exposing the cans to superheated steam ranging in temperature from 226° F. to 245° F. Either while the evaporation is in progress, or later in the process, the cans are shaken to convert their contents into a smooth product.

266. Sweetened Condensed Milk is required to contain at least as large a percentage of milk sugar and milk solids as evaporated milk. In place of sterilization, sufficient cane sugar is added to prevent fermentation. The amount of cane sugar used is about 40 % of the product (Fig. 88). Unsweetened condensed milk is superheated in the vacuum pan by blowing live steam into it.

267. Advantages of Condensed Milks. — A high grade of raw milk is taken to start with, and the natural milk solids and fat are retained in the condensed milk, while the volume of the milk is greatly reduced, and the cost of transportation correspondingly lessened. Both evaporated milk and sweetened condensed milk can be kept for many months without undergoing appreciable change. They may consequently be prepared in remote rural districts where milk is cheap, and be transported to cities where the demand for milk is great. By the addition of water, evaporated milk of good quality may be converted into a product that is superior to the poorer grades of milk often sold in large cities. These facts are causing condensed milk to be used in increasing quantities.

268. Powdered Milk. — Many attempts have been made to remove practically all of the water from milk, and reduce the total milk solids to a powder. Some of these have been so successful that several brands of powdered milk are at present on the market. One of the most ingenious methods employed consists of first condensing the milk in a vacuum pan, and then spraying the still fluid milk under high pressure through fine nozzles into an inclosed room, and against a current of hot air. It has been estimated that one pint of milk in the form of the spray presents about two acres of surface. The moisture still remaining in the milk is almost instantly absorbed by the hot air and the milk solids fall. When whole milk is used, the milk powder obtained from it has good keeping properties, and when skimmed milk is employed, the powder will keep still better. The milk obtained by the addition of water to powdered milk is wholesome and of fair quality. It is excellent for use in cooking. Powdered milk when dissolved in water furnishes an ideal medium for the culture of lactic acid bacteria, as it is thoroughly sterilized and can be inoculated with pure cultures.

269. Homogenized Milk is milk that has been forced through minute openings under a tremendous pressure reaching approximately from 1500 to 3000 pounds to the square inch. The fat globules are broken and evenly distributed through the milk so that an excellent emulsion is obtained from which the fat does not separate readily. It is possible to incorporate sweet butter with skimmed milk, or powdered milk, by the process of homogenization. Homogenized milk is always thicker than the milk from which it was made, and appears to contain more fat than is actually the case. It has been sold by dairymen as cream. While homogenized milk furnishes a pleasing article to use in tea or coffee, it is impossible to convert it into whipped cream. It is fraudulent to sell homogenized milk as cream. Ice cream manufacturers use homogenized milk in large quantities.

270. Fermented Milks of various kinds have been highly esteemed for centuries by people of different nationalities. In this country, buttermilk has long been considered a health-producing and, by many, a delicious drink. Buttermilk is that portion of the cream that is left after the removal of nearly all of the milk fat during the process of churning. As the cream is generally permitted to sour before being churned, the buttermilk contains a small amount of lactic acid. The wholesome qualities of buttermilk are thought to be due chiefly to lactic acid bacteria.

Within recent years a considerable number of brands of fermented milks and of cultures for their production have been placed on the market under such names as Zoolak, Lacto-Bacilline, Vitallac, Kumiss, Fermilac, etc. These preparations have come to be well thought of as correctives for intestinal disorders. As it is difficult in our large cities to obtain a satisfactory buttermilk, tablets and capsule cultures for the preparation of artificial buttermilk from sweet milk have become articles of commerce. These contain more or less pure cultures of lactic acid producing bacteria and are accompanied by directions for the preparation of a fermented milk. After the milk has been pasteurized at a high temperature, it is inoculated, and is then kept at a temperature suitable for the growth of the bacteria used, until the desired degree of acidity has been attained. The process is then stopped by lowering the temperature of the product to a point below that at which the bacteria grow. The ordinary lactic acid producing bacteria are likely to cause the casein of the milk to precipitate and settle, leaving on top a clear liquid, the whey. Most of the fermented milk on the market is made from skimmed milk.

Recently cultures of ***Bacillus bulgaricus***, for use in bringing about lactic acid fermentation in milk, have been placed on the market. This ferment differs in several respects from the ordinary lactic acid bacteria. It does not cause the casein to separate from the whey; it produces a higher percentage of lactic acid and thrives at a higher temperature than the ordinary lactic acid bacteria. A temperature of 100° F. is best adapted to the growth of ***Bacillus bulgaricus*** and the lower temperature of 70° F. is best for the growth of the ordinary lactic acid bacteria. The ***Bacillus bulgaricus*** also survives the digestive operations of the stomach and is carried into the intestines, where it continues to produce lactic acid. Both for this reason and because it thrives well at the body temperature, the ***bulgaricus*** is considered the best lactic acid bacillus for making sour milk preparations.

Kumiss probably originated in Asia, where the term was applied to fermented mare's milk. In this country, a fermented milk sold as Kumiss is made from cow's milk. The best results are said to be obtained by bringing about an alcoholic fermentation in a good quality of buttermilk to which cane sugar has been added. Yeast is used to ferment the sugar, causing the production of alcohol and carbon dioxide. The carbon dioxide imparts to the Kumiss the sharp taste of a plain soda and produces a desirable effervescence.

SUMMARY

Milk is such a common article of diet that its purity is essential to the health of the community. The disease germs that milk contains are not likely to be killed before the milk is used.

Typhoid fever, scarlet fever, and diphtheria are some of the forms of disease that are known to be occasioned by the use of infected milk.

The Bacterial Content of milk increases with tremendous rapidity between 80° F. and 100° F. Below 50° F. there is practically no increase in the number of bacteria present.

Souring of milk is brought about by forms of bacteria that convert milk sugar into lactic acid. The growth of **Putrefactive Bacteria** that produce dangerous poisons (ptomaines) in milk is held in check by bacteria that form lactic acid. Many of the putrefactive bacteria produce spores that are not readily killed by heat.

Preservatives in the form of deleterious chemicals, such as formaldehyde and borax, should never be used to keep milk sweet.

Pasteurization of milk consists in heating milk to a temperature of from 145° F. to 167° F., holding it between these temperatures for 20 minutes, and then quickly cooling it. Nearly all the bacteria that produce diseases are killed by this treatment, but the milk is not sterilized. Pasteurized milk should be kept at a temperature between 40° F. and 50° F. until needed for use.

Certified Milk is supposedly produced according to rules formulated and enforced by a milk commission. The label " certified " depends for its value upon the integrity of the milk commissioners.

Modified Milk is cow's milk, the composition of which has been changed to make it more closely resemble mother's milk. The change should be based upon analyses made by a competent milk chemist.

Sterilized Milk is free from living organisms. It is prepared by treating raw milk so as to destroy all bacteria and their spores. Such milk will remain sterile if not permitted to come in contact with air, or if it contains some poison which will kill any germs that may reach it.

Evaporated Milk differs from **Sweetened Condensed Milk** in that no sugar is added to the former during its preparation. Both are prepared by evaporating the water from milk until the residue has the consistency of thick cream.

Powdered Milk is produced by removing the water from raw milk and converting the milk solids into a powder.

Homogenized Milk is made by the use of enormous pressure to force raw milk through minute openings. The process breaks the fat globules and thickens the milk.

Fermented Milks are produced by inoculating raw milk with forms of bacteria believed to produce changes which make the product more wholesome than ordinary milk.

EXERCISES

1. Why is a bountiful supply of pure milk essential to the health of the community?

2. Compare the average composition of cow's milk with mother's milk.

3. What is the highest content of water, the lowest content of fat and total solids permitted in milk legally offered for sale in New York City?

4. Briefly tell about some of the ways in which disease germs enter milk.

5. Why is it desirable that milk carried from the country to large cities should be kept at a temperature between 40° F. and 50° F. while in transit?

6. What causes milk to sour?

7. What are some of the methods employed to keep milk sweet?

8. Which of the methods employed to keep milk sweet is the most desirable?

9. Is a sweet milk always a safe milk to use? Explain.

10. What are the advantages of pasteurized milk?

11. How does pasteurized milk differ from sterilized milk?

12. Why is it essential that pasteurized milk be kept cool until required for use?

13. Under what conditions may pasteurized milk be more dangerous to use than raw milk?

14. What is certified milk?

15. Does the fact that a milk is certified necessarily mean that the milk is safe to use?

16. What is modified milk?

17. Why is it impossible to give definite general directions for the correct modification of cow's milk?

18. Distinguish between evaporated milk and sweetened condensed milk.

19. What is powdered milk?

20. How is milk homogenized?

21. How does homogenized milk differ from cream when whipped?

22. Mention some of the names given to fermented milks.

23. What advantage is there in the use of *Bacillus bulgaricus* instead of the ordinary lactic acid bacteria?

24. Why is Kumiss effervescent?

CHAPTER XXV

CREAM, ICE CREAM, BUTTER, AND CHEESE

271. Cream. — Milk is a solution that contains in suspension globules of fat and also particles of casein which are in chemical combination with calcium. When fresh milk is allowed to stand for some time, the fat globules gradually rise to the top of the milk and form a layer rich in fat. This layer is the cream. As the process of obtaining cream by allowing the milk to stand is too slow for the modern dairy, *separators* are generally used to separate the cream from the remaining portions of the milk. A separator is a centrifugal machine in which the milk is made to rotate rapidly. The cream, being the lighter portion of the milk, collects near the axis of rotation, while the heavier portions are thrown toward the circumference. Cream should contain at least 18% of fat.

When cream is beaten with some implement, such as an egg beater, the clusters of fat globules are broken and, before the fat collects in the form of butter, the cream thickens so that the particles of air which become entangled are held, producing a foam which is known as *whipped cream.* Cream that has been recently heated does not whip readily. The viscosity may be restored to such a cream by allowing it to remain in a cool place for a few hours, or by the addition of a solution known as "Viscogen." This is prepared by slaking 1 part of lime in 3 parts of water and adding to the slaked lime 2½ parts of sugar dissolved in 5 parts of water. The mixture is shaken at intervals during 2 or 3 hours, after which it is allowed to settle and the clear liquid is siphoned off. From 1% to 1½% of "Viscogen" is added to the cream. Cream should be at a low temperature (40° F. to 50° F.) when whipped.

272. Ice Cream is popularly supposed to be a frozen mixture of cream, sugar, and flavoring material, to which may have been added some artificial color. As a matter of fact, it often differs widely from such a mixture. In addition to the articles mentioned, several other substances are commonly used in making ice cream. Eggs and a considerable portion of milk are often used in the homemade article. Such a product is really a frozen custard. Gelatin is in many instances added to give firmness, so that, when served, the pieces do not lose their shape readily. Gum tragacanth furnishes a desirable substitute for gelatin. Corn starch and flour are other substances frequently used as binders.

Ice cream made by freezing a mixture of pure, rich cream, sugar, and flavoring material contains too much fat to be easily digested by many people when the usual quantity is eaten, and so is objected to on account of its "richness." On the other hand, ice cream low in milk fat has a coarse, granular structure, due to the crystals of ice that separate from the mixture. Ice cream containing from 14% to 18% of fat is considered to be best for general use.

The use of coal tar dyes as coloring matter for ice cream is both unnecessary and unwise. Ice cream is most extensively used during the summer months when plenty of fresh fruits may be obtained for flavoring materials. These give the finished product unexcelled flavors and pleasing colors. It is better to add the fruit at the time the ice cream commences to thicken in the freezer, otherwise the fruit acids may cause the cream to curdle, and the fruit is likely to be frozen too hard.

All that has been said in the preceding chapter concerning the dangers arising from the use of impure milk, applies with greater force to impure ice cream. Dr. Wiley states that 263 samples of ice cream, which were collected and examined, in one of our large cities, contained on the average over 26,000,000 organisms per cubic centimeter, and that 16 of the samples contained 100,000,000 per cubic centimeter. Of the 115 samples examined for disease-producing bacteria, 38.3 % were found to be infected. The popularity of ice cream as an article of food during the summer months, together with the fact that a considerable portion of the ice cream sold is eaten by children, should cause the people to demand the enactment and enforcement of stringent laws governing its manufacture, storage, and sale. At present, the consumer seldom knows what the ice cream he purchases contains, under what conditions it was made, where it has been stored, or the cleanliness of the persons who have handled it.

273. Butter. — When cream is beaten or agitated for some time, the fat globules are broken down and the fat crystals collect in lumps of butter. The butter is washed with water, and "worked" to squeeze out the buttermilk which has remained entangled between the particles of fat. The product thus prepared may be sold directly as *unsalted* or *sweet butter*, or it may be thoroughly mixed with salt and sold as butter. Unsalted butter has poor keeping qualities, while good salted butter keeps well in a clean, cool place. Good cream, great care in preparation, non-porous containers, a cool place free from odors, and cleanliness from beginning to end are essential to the keeping qualities of butter. Poor butter is one of the most common articles of commerce.

274. Process or Renovated Butter. — The fact that much of the butter placed on the market soon becomes rancid has led to the development of methods for the conversion of "strong" butter into a substance closely resembling fresh butter. One process employed for this purpose is essentially as follows:

The rancid butter is taken to the factory, where it is dumped into a melting vat. The clear, molten fat is strained and then raised to a temperature of 120° C. After the curd has settled and has been separated, streams of air are passed through the warm oil for several hours. The air removes disagreeable odors and produces a clear, nearly tasteless oil, which, after being churned with a mixture of sweet and sour buttermilk, is gathered and salt is worked into it.

275. Adulterated Butter. — This term has been applied to all mixtures of butter with cheaper fats and to all substitutes for butter. The adulteration of butter with the purpose of deceiving the consumer has been prohibited by law. At present, very few persons are deceived by the purchase of spurious butter. The term adulterated butter should not be applied to oleomargarine, butterine, renovated butter, and similar preparations sold under their true names.

276. Oleomargarine and Butterine. — These and similar preparations are sold extensively as substitutes for butter. Oleomargarine is said to have originated through the efforts of a French chemist, Mège-Mouries, to furnish the poorer classes and sailors of France with a cheap and otherwise desirable substitute for butter. He tried to make butter by an artificial process. His first description of a method for making imitation butter on a large scale appeared in 1870. A patent for the manufacture of an artificial butter was granted by the United States in 1873, and since that time many other patents have been issued for the manufacture of substitutes for butter.

In general, oleomargarine consists of various mixtures of fats. These are beef fats of various kinds, neutral lard, cottonseed oil, and palm oil. The mixtures are agitated with milk, which has generally been soured with pure cultures of lactic acid bacteria, and then colored and salted, so that the product very closely resembles butter. *Butterine* differs from oleomargarine in that it contains a certain percentage of butter.

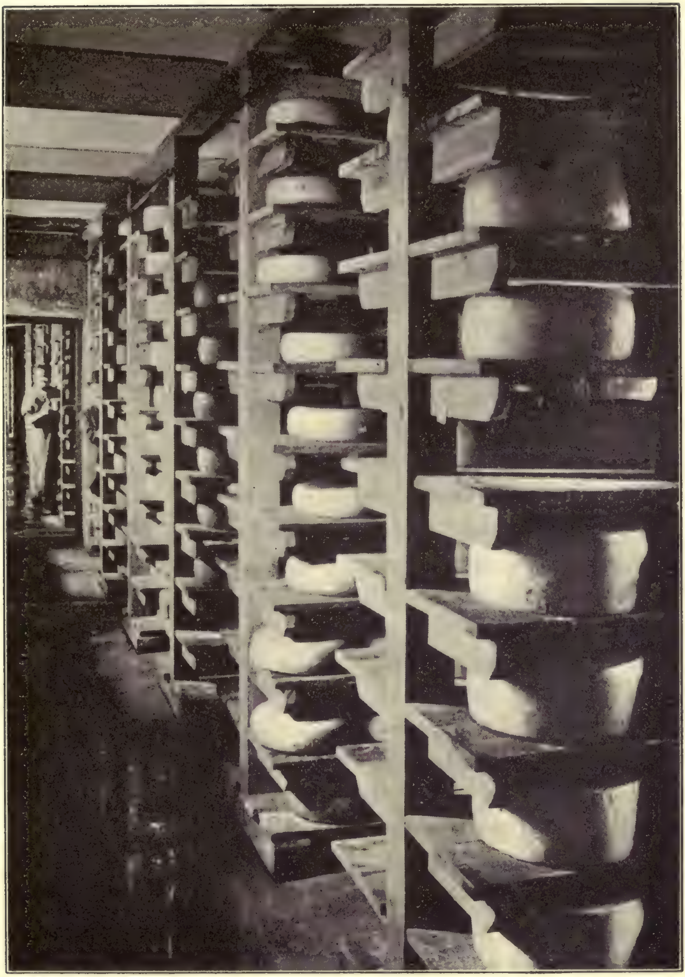
Great care and cleanliness are exercised in the preparation of artificial butters and they are generally considered wholesome, though not so desirable as pure butter for frying, or for table use, on account of the unpleasant odor on hot food.

277. Cheese is made by curdling milk by means of a dilute acid, or by the ferment contained in rennet, and then bringing about desirable flavors by the addition of salt and, especially, by permitting various organisms to act upon the curd. An herb, for example, sage, is sometimes used for additional flavoring material.

278. Cottage Cheese, schmierkäse, Dutch cheese, sour milk cheese, and Philadelphia cream cheese are various names applied to a cheese produced by the action of lactic acid bacteria on milk. In the home, the usual method employed for making cottage cheese is to let the milk sour until a thick curd has formed. The curdled milk is heated to about 100° F. and stirred until the whey appears clear. Then the product is placed in a cheesecloth bag which is hung so that the whey will drain off. The moist curd is then mixed with sufficient salt and cream to give the product the desired flavor and richness.

When cream cheese is manufactured on a large scale, a rapid souring of sweet skim milk is brought about by the use of pure cultures of lactic acid bacteria. The curd produced is separated and then treated in a manner similar to the homemade article. Cream cheese does not keep well.

279. American Cheese. — A ferment that is extremely active in curdling milk is produced in the fourth stomach of the calf. *Rennet* is the commercial name for a preparation of this ferment. The active principle (enzyme) of rennet is so powerful that 1 part of rennet will bring about the desired change in 400,000 times its weight of casein. Rennet is commonly used in making cheese from sweet milk. The process may be briefly outlined as follows: sweet skimmed milk is heated to about 86° F. and the rennet added. After the curd has formed, the whey is allowed to sour, in order to bring about a more complete separation of the curd. The curd is collected, freed from whey, salted, and pressed. The fresh ("green") cheese is then allowed to ripen, that is, it is allowed to stand until processes of fermentation have brought about the desired flavor (Fig. 89). Several months were formerly required for a cheese to ripen satisfactorily. Artificial processes for producing a flavor similar to that of a well-ripened cheese have been introduced in cheese factories, so that the time required for the conversion of the "green" cheese into a palatable product has been greatly lessened. The richness of the cheese varies greatly with the amount of cream contained in the milk from which it was made, and with the amount of fat rubbed over the cheese during the process of ripening.



Copyright by Underwood & Underwood, N. Y.

FIG. 89. — RIPENING OF CHEESE.

Other varieties of cheese are too numerous to be mentioned in an elementary book. They are made from the milk of either the cow or the goat. Their flavor and consistency differ greatly with the kind of organisms that take part in the process of ripening.

Cheese is a highly nitrogenous substance, the food value of which is not generally appreciated.

SUMMARY

Cream consists of the fat globules which rise slowly and form a layer on top of milk.

Separation of the Cream from the remainder of the milk is brought about rapidly by the use of a centrifugal machine, called a separator.

Whipped Cream is the foam produced by beating cream until the fat globules are broken and mixed with air.

Ice Cream is generally supposed to be a frozen mixture of cream, sugar, and flavoring material. Almost any frozen custard, or milk thickened by the use of gelatine, or gum tragacanth, sweetened, flavored, and frozen, passes for ice cream.

The Manufacture and Handling of Ice Cream should be conducted with a high degree of cleanliness, as ice cream furnishes a rich culture medium for disease-producing bacteria.

Sweet Butter is made by agitating cream until the fat globules are broken and the crystallized fat has collected in lumps. The fat is then washed and worked, to squeeze out the buttermilk that has remained between the particles.

Butter is sweet butter that has been mixed with salt.

Process or Renovated Butter is made by converting rancid butter into a product closely resembling fresh butter.

Oleomargarine is a general name applied to artificial butters.

Butterine differs from oleomargarine in that it contains some butter.

Cheese is the protein of milk obtained by curdling milk with an acid or more generally by the ferment of rennet. Desirable flavors are produced by salt, bacteria, and other organisms.

EXERCISES

1. What is cream?

2. Why are separators used in modern dairies?

3. What is the lowest percentage of fat that should be present in cream?

4. What is whipped cream? How should cream be treated preparatory to being whipped?

5. What is "Viscogen"?

6. What is ice cream?

7. Why should great cleanliness be exercised in the manufacture and handling of ice cream?

8. Why should the use of dyes in the making of ice cream be discouraged?

9. Why should stringent laws regulating the manufacture, handling, and sale of ice cream be enacted and enforced?

10. What advantage would there be in requiring that the formula used in making the ice cream be furnished to the purchaser on request?

11. How is butter made?

12. How does sweet butter differ from butter?

13. What is process or renovated butter?

14. What is oleomargarine?

15. How does butterine differ from oleomargarine?

16. Why should not oleomargarine be called adulterated butter?

17. What advantages are there in the use of oleomargarine, or butterine, instead of butter? What disadvantage?

18. What is cheese?

19. How is cottage cheese made?

20. Briefly describe the manufacture of American cheese.

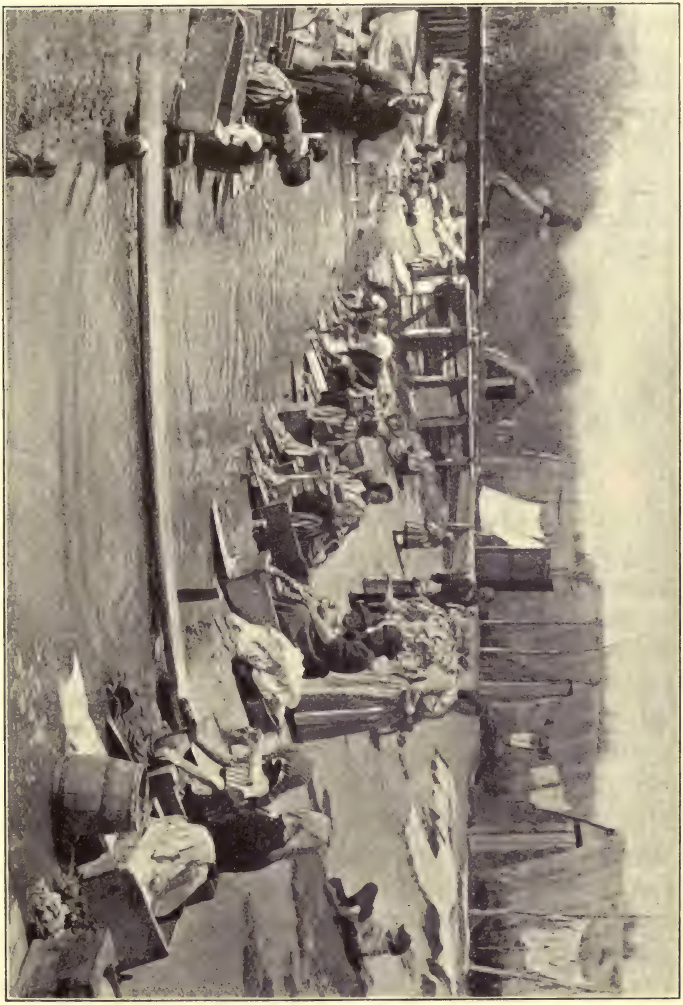
CHAPTER XXVI

CLEANING AND LAUNDERING

280. The Nature of the Cleaning Process. — The operations of cleaning frequently involve both physical and chemical processes. Dirt, which is, after all, only *matter in the wrong place*, can sometimes be removed by the mechanical means of brushing, shaking, or agitation with water, the object being to first loosen the dirt by friction and then carry it away by currents of air or water (Fig. 90). Usually, however, there is enough greasy matter present to cause the dirt to adhere so that these means alone are not effective. In such cases a substance must be used that will dissolve grease. Soap is employed ordinarily to accomplish this end.

281. Soap. — All the strong bases, such as sodium and potassium hydroxides, have the power of acting chemically on fats and greases. They cannot often be used directly as cleaning agents, however, because they are extremely caustic and act readily on all sorts of organic matter. For cleaning floors, greasy ironware, or sinks, solutions of bases may be used, if the person who handles them is careful not to get them on his flesh or clothing. But for ordinary cleaning operations we must use the highly modified bases which we call *soaps*. These also have the power of dissolving fats or grease, but, if pure, they are not caustic in their action on the skin and fabrics.

282. The Manufacture of Soap. — The essential step in the manufacture of soap is a chemical action between a strong



Copyright by Underwood & Underwood, N. Y.

FIG. 90. — PRIMITIVE WASHING IN SPAIN.

base and a fat. Fats are organic salts, analogous to inorganic salts like sodium sulphate, Na_2SO_4. For example, beef fat is mainly glyceryl stearate, $C_3H_5(C_{18}H_{35}O_2)_3$; the part of a metal is played by the glyceryl radical, C_3H_5; the acid radical, $C_{18}H_{35}O_2$, is that of stearic acid, $HC_{18}H_{35}O_2$. Other fats are mixtures of glyceryl salts. The main acid constituent may be from oleic, palmitic, or some other acid. When any of these fats is boiled with sodium hydroxide, a soap and glycerin result from the action:

$$\underset{\substack{\text{glyceryl}\\ \text{stearate}\\ \text{(fat)}}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{3\,NaOH} \longrightarrow$$

$$\underset{\substack{\text{sodium}\\ \text{stearate}\\ \text{(soap)}}}{3\,NaC_{18}H_{35}O_2} + \underset{\substack{\text{glyceryl}\\ \text{hydroxide}\\ \text{(glycerin)}}}{C_3H_5(OH)_3}$$

In the actual manufacturing operation, the boiling of soap is often carried out in huge kettles that will yield 20 to 30 tons of the product. The operation lasts from several hours to two or three days. At the end of this period, common salt is added. Soap is insoluble in brine, and hence separates and rises to the top of the kettle. The salty liquid at the bottom is drawn off, and in most cases is distilled under diminished pressure to obtain the glycerin which it contains. The "salting out," as it is termed, also affords a means of getting rid of the excess of base that would otherwise remain in the soap.

Laundry soaps are made from animal fat, refuse fat from the kitchen, palm oil, and cottonseed oil. Cocoanut oil can be made into a soap by a "cold" process, provided that a carefully calculated quantity of base is used. In this soap the glycerin remains in the finished article.

If potassium hydroxide is used as the base, a soft soap results. "Green soap" and shaving soap are potassium soaps, at least in part. Floating soaps are obtained by beating air into the product before allowing it to harden. Castile soap is made from an inferior grade of olive oil.

283. Quality of Soap. — This depends chiefly on two factors. One of these is the use of a fat that is fairly pure and that will not become rancid in the soap; the other is the avoidance of an excess of base, which, if present, makes the soap caustic and injurious to the skin and fabrics.

284. Adulterations in Soaps. — Soaps are very much subject to adulteration. *Sodium silicate*, a cheap substance which has a certain amount of cleansing power, is frequently used for this purpose. Its use is undesirable; it is injurious to fabrics and it tends to make the soap retain a high proportion of water. This makes the soap deceptive in bulk and makes it waste very rapidly in use. *Rosin* is nearly always added to laundry soaps and is the reason for their yellow color and strong lathering properties. Used in proper quantity rosin is not an adulterant, because it combines with the base and makes a rosin soap, and the formation of lather plays an important part in the cleaning operation. *Water* is considered an adulterant in soaps when present in quantities above 25%. It makes the soap soft, so that it wastes rapidly. Many other substances are used in adulterating soaps. Almost anything that is cheap and bulky is used for the purpose. Toilet soaps are frequently adulterated with substances of supposed medicinal value.

285. Special Soaps. — The only requirements for good toilet soaps are that they be made from purified fats, and that they do not contain an excess of base. This latter requirement is particularly necessary, since the caustic base would roughen the skin. Castile soap, when good, makes a thoroughly satisfactory toilet soap.

Powdered Soaps. For toilet purposes these are made by simply grinding a thoroughly dried toilet soap of good quality. For laundry purposes, the trimmings of cake soap are used, and soda ash (sodium carbonate) is nearly always added.

Shaving Soaps. The strong lathering properties of these soaps are secured by addition of rosin and they are always potassium soaps in part. Sometimes they are made from cocoanut oil with the addition of stearic acid.

Liquid soaps are less used than powdered soaps.

Scouring soaps are made from laundry soaps by addition of ground quartz, pumice, or other abrasive. They are dried in molds.

286. Other Cleaning Agents. — *Washing soda*, Na_2CO_3, *sodium carbonate*, resembles strong bases like sodium and potassium hydroxides in its chemical properties, but is much more moderate in its action. A strong solution, however, is injurious to the hands and fabrics. But its power to dissolve grease makes it a great aid in cleaning coarse or very dirty articles, and its use for this purpose is not objectionable, especially if the washing is done in a machine.

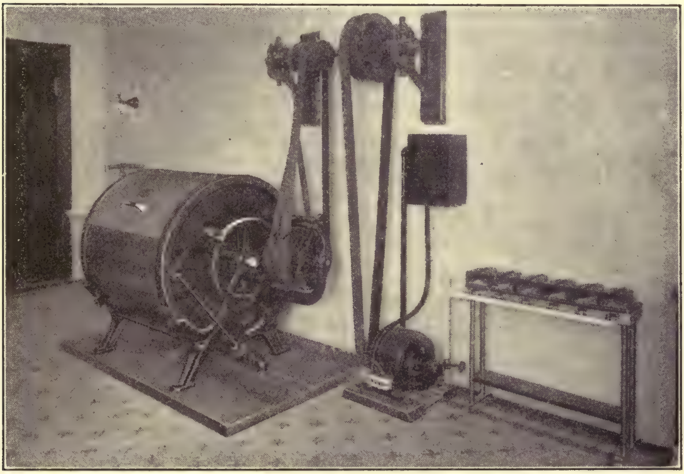
Borax, $Na_2B_4O_7$, a substance that is found ready made in nature, represents a still more moderate form of alkali, but one that also has the power of dissolving grease. It is a very valuable cleaning agent, and it will cleanse even a very dirty cloth to clear whiteness. Its use is somewhat limited owing to its comparative high cost.

Ammonia water, ammonium hydroxide, NH_4OH, which is practically a solution of ammonia, NH_3 in water, also acts like sodium hydroxide, but with moderated intensity. It is particularly valuable because it is volatile. Its solution breaks up into its constituents according to the equation:

$$\underset{\text{ammonium hydroxide}}{NH_4OH} \longrightarrow \underset{\text{ammonia}}{NH_3} + \underset{\text{water}}{H_2O}$$

A strong solution may be applied directly to the clothing because it evaporates in a few minutes and does not remain in contact with the goods long enough to affect it harmfully. It is useful for removing grease spots from the clothing.

287. Washing. — The first step in the laundering of clothes is the combined action of vigorous mechanical agitation and the solvent power of soap solution. In laundries, and increasingly in homes, work formerly done



Copyright by Underwood & Underwood, N. Y.

Fig. 91. — An Electric Laundry.

by hand is now done by washing machines (Fig. 91). These machines save a great deal of labor and give very satisfactory results. White materials of strong texture will stand vigorous treatment; a small amount of washing soda and a high temperature are quite helpful. Colored fabrics must be handled more carefully. Kerosene oil, which is an excellent grease solvent, is added to the hot soap solution with good results. Thorough rinsing is needed to remove all soap from the garments.

288. Bluing. — The next step in the laundering of white goods is bluing. The soap and heat used in washing have a tendency to develop a yellow tint. Blue is the complementary color to yellow, and a treatment of the goods in a bath of a blue color neutralizes the yellow tint. Various blue dyes, and the pigments, Prussian blue and ultramarine, are used for the purpose. The pigments are preferred because they have less tendency to accumulate in the cloth with successive washings. Ultramarine is better than Prussian blue, owing to the fact that the latter is an iron compound which reacts with bases or alkalies to form ferric hydroxide:

$$\underset{\text{prussian blue}}{Fe_4[Fe(CN)_6]_3} + \underset{\text{sodium hydroxide}}{12\ NaOH} \longrightarrow$$

$$\underset{\text{ferric hydroxide}}{4\ Fe(OH)_3} + \underset{\text{sodium ferrocyanide}}{3\ Na_4Fe(CN)_6}$$

Hence red spots of what is practically iron rust sometimes develop on clothing that has been blued with Prussian blue. If this happens, it is because all of the soap was not rinsed from the clothes before they were put in the bluing water.

289. Starching. — Starch is used to make garments stiff, and also to keep them clean longer. It is applied both cooked and uncooked. Starch is found in many plants. The microscope shows that it is composed of granules or cells. When starch is boiled with water, these cells burst open and the cooked mass acquires a gelatinous character. This characteristic makes it adhere firmly to the goods after it has been worked into the fibers. For starching collars, uncooked starch is used, probably for the reason that the goods will take more starch cells in this condition. During the ironing, the starch becomes at least partly cooked and thus acquires the desirable gelatinous quality and gloss.

290. Dry Cleaning. — Gasoline and benzene are organic liquids much used for cleaning purposes because they are powerful solvents for grease and are also readily volatile. With their aid we can cleanse fabrics that will not stand the use of soap and water. Silk and woolen goods are best cleaned in this manner. The solvent immediately dissolves any oily matter that is present and the dirt is carried away by the currents of liquid that flow through the fibers.

GREAT DANGER attends the use of gasoline in cleaning. This is due to the fact that this inflammable liquid is so volatile that if it is used in any closed space, such as a room, the air very quickly contains a considerable quantity of the solvent in the form of a gas. The mixture of oxygen and hydrocarbon vapor is *highly explosive.* A light or spark, no matter how small, is enough to set it off. Serious accidents have happened from the common, but erroneous, belief that it is the liquid gasoline which is explosive. It is not the liquid, but the mixture of *air* with *gasoline vapor*, that is dangerous.

All cleaning with gasoline or other volatile, inflammable liquid should be carried on out of doors, or in a room through which a strong draft of air is blowing. Any possibility of enough of the gas collecting to form an explosive mixture, is thus avoided.

291. Spots and Stains. — Where ordinary washing or solvent action does not suffice, special chemical treatment is necessary to remove spots and stains. Methods for the removal of various kinds of stains may be classified under certain general principles.

Neutralization is used when the spot is due to either an acid or a base. For acids, ammonium hydroxide is applied. Bases should be treated with a weak solution of acetic acid (vinegar), and the excess of the acid neutralized with ammonium hydroxide. *Bleaching* is employed where the spot has been formed from the action of a dye or of fruit juice. *Javelle water*, an alkaline solution that readily liberates chlorine, is useful for this purpose, or sulphur dioxide may be used where chlorine would be too active, as in the case of silk or wool.

Ink stains are often removed by a *reducing* agent. Most inks contain ferrous tannate which on exposure to air becomes ferric tannate. The latter is a substance which gives to ink its final black color. By the action of a reducing agent, such as oxalic acid, the ferric tannate is again changed to a ferrous compound which is soluble and can be washed away. The primary dye that is in the ink may remain and require removal by bleaching with a solution of bleaching powder acidified with oxalic acid. In removing spots it is well to first test a small piece of the goods with the agent that it is proposed to use, in order to make sure that neither the dye nor the fabric will be injured.

292. The Use of Bleaching Agents in Laundering. — In commercial laundries it is not uncommon to make use of bleaching solutions to hasten the operation of cleaning. This is not desirable, since repeated use of such solutions tends to disintegrate the cloth. Chlorine is frequently used to accomplish the bleaching. It can be obtained from chloride of lime, CaO_2Cl_2, by the addition of dilute acid. A process for obtaining chlorine by the electrolysis of sea water (brine) is rapidly coming into use. Javelle water is also used as a source of chlorine. It is prepared by treating chloride of lime with sodium carbonate, Na_2CO_3 (washing soda), or potassium carbonate, in water solution.

SUMMARY

In Cleaning it is first necessary to remove oily or greasy matter that causes the dirt to adhere to the soiled article. Soaps are used because they are good solvents for grease and are themselves soluble in water.

Soaps are made by boiling solutions of strong bases, usually sodium hydroxide, with fats or oils. The soap, which is the sodium or potassium salt of a fatty acid (stearic, palmitic, oleic), and glycerin result from the action.

Toilet Soap should not contain any free base, nor more than 25 % of water.

Laundry Soaps are made with the addition of rosin during the operation of boiling. This gives them strong lathering properties.

Special Soaps and Cleaning Powders generally contain sodium carbonate, which makes them rather caustic in action. Borax, which is not so caustic as the sodium carbonate, is also used.

Scouring Soaps are made from ordinary soap by the addition of a powdered abrasive such as pumice or quartz.

Washing Soda, Ammonia Water, or Borax can be used where a stronger grease solvent is desired than that which can be obtained by the use of soaps.

The Operation of Washing is dependent on the solvent action of the soap solution plus the mechanical action of moving currents of water.

Bluing is used to neutralize the yellow tint which washing develops in white goods. Dyes, Prussian blue, or ultramarine are used. The last-named substance is the best.

Starching stiffens clothes and makes them keep clean longer.

Dry Cleaning is accomplished with organic solvents that evaporate quickly from the cloth. They act in the same way as water except that they themselves are good grease solvents.

Gasoline and benzene are the substances most used for dry cleaning.

The use of these inflammable liquids for cleaning purposes is very dangerous. A mixture of their vapors with air is highly explosive and can be set off by a minute spark or flame at some distance from the place where the cleaning is being done. Such work should be done out of doors.

Spots and Stains require special chemical treatment according to the nature of the spot.

EXERCISES

1. How does water act mechanically in cleaning operations? What part does soap play?

2. Would gasoline and water make as satisfactory a combination for cleaning the hands as soap and water? Explain.

3. Explain the process of making soap. Why is there frequently free base in finished soap? How can this be avoided?

4. Is there any objection to free base in toilet soap? Why? In laundry soap? Explain.

5. Is a lathering property desirable in soaps? Why? How is it obtained?

6. Why is it not desirable to have more than 25 % of water in soaps?

7. Name some adulterants commonly used in soaps. Why is their use objectionable?

8. "Medicated" soaps are usually sold at a higher price than ordinary good toilet soaps; is this extra price justifiable?

9. What is the chief difference between sodium soaps and potassium soaps? For what purposes are potassium soaps desirable?

10. What is a scouring soap? From the standpoint of economy, what could you substitute for these with advantage for rough cleaning?

11. Why is ammonia water useful in cleaning? What advantage has it over soap? Over washing soda?

12. Which is preferable for cleaning purposes, washing soda or borax? Discuss.

13. What advantage is there in the use of a washing machine for laundry work?

14. If iron rust spots appear on clothing after washing, what operation in the washing process may have caused them? How would you avoid trouble of this sort?

15. Why does a change take place in the appearance of a mixture of starch and water as it is being cooked? How is starch applied for making collars, etc., very stiff?

16. What kinds of goods are best cleaned by dry cleaning? Why?

17. Explain the process of dry cleaning.

18. State precautions to be observed in the use of gasoline for cleaning purposes. Give reasons.

19. How would you remove a grease spot from a woolen suit? An acid spot?

20. What is Javelle water? How is it made? Why is it useful in the household? Why should this solution not be allowed to remain long in contact with cloth? How would you counteract its undesirable effects?

CHAPTER XXVII

INK

293. Writing Inks may be roughly divided into three classes: those whose color depends on iron salts of one or more of the tannic acids, or tannins; those whose color is due to an aniline dye; and those whose color is due to finely divided carbon.

Tannin and tannic acid are terms applied to a class of substances that are soluble in water, possess a bitter, astringent taste, and have the property of converting the skins of animals into leather. They react with ferric salts to produce a nearly black precipitate. Many plants yield tannins, and the tannin is generally named from the plant producing it. Thus we have chestnut tannin, oak bark tannin, and sumac tannin.

294. Galls are morbid growths produced on many plants when their twigs are punctured by insects. These partake more or less of the nature of the plant on which they grow. One variety of such growths has for many years been of importance in the manufacture of ink. An insect, commonly called the gall-insect or gall-fly, pierces the tissue of the branch of an oak tree, and deposits an egg together with a small quantity of a poisonous fluid in the cavity. The fluid causes a growth, known as a gall, to develop rapidly, and in this the egg hatches and the insect matures. The mature insect finally eats its way out of the gall and flys away. Oak-galls, or nutgalls as they are called, are articles of commerce. They are globular in shape and are generally about half an inch in diameter (Fig. 92). Galls that have not been punctured are considered by ink manufacturers to be of superior quality. Good nutgalls are quite compact and heavy. The tannic acid derived from nutgalls is known as *gallotannic acid*. A good quality of nutgalls yields about 25% of tannic acid. The acid can be obtained from finely pulverized galls by soaking the powder in ether and then filtering, in order to separate the solution of the acid from the insoluble mass, and then evaporating the solution to dryness. When boiled with water, the tannic acid combines with the water and forms gallic acid; that is, tannic acid is the anhydride of gallic acid. When an aqueous solution of tannic acid is allowed to remain exposed to the air, a process of fermentation takes place and it is converted into gallic acid. A number of other tannic acids, and also gallic acid itself, are used in the manufacture of inks.

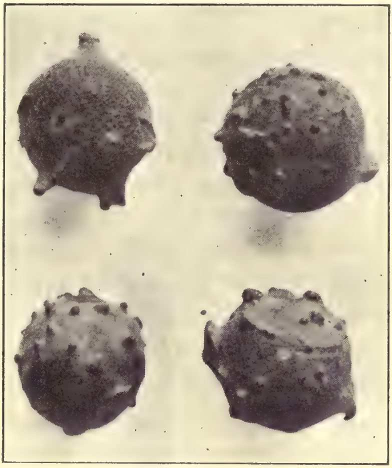


FIG. 92. — NUTGALLS, ACTUAL SIZE.

295. Iron Inks. — When a water solution of pure ferrous sulphate is added to a water solution of tannic acid, a colorless solution results (Fig. 93, *a*). If this colorless solution is brought in contact with an oxidizing agent, for example, hydrogen peroxide, the fluid immediately changes to a black color. This change is due to the fact that while the ferrous salts of the tannic acids are soluble in water, the ferric salts of many of them are black and insoluble. When the colorless solution referred to above is exposed to air, oxidation takes place slowly (Fig. 93, *b*), and the consequent blackening occurs less rapidly. This slow oxidation may be further hindered by the addition of a few drops of some strong acid, for example, sulphuric acid. When a solution of ferrous tannate is used as an ink, the writing is at first nearly invisible, but on exposure to air, oxidation takes place and the writing becomes black. In order that the writing may be visible when the ink is first applied to the paper, some pigment, such as indigo carmine, is added to the ink. This gives ink a blue-black color when first applied, and this color is later changed to black by the oxidation of the ferrous tannate. To cause the ink to adhere to the pen and thus prevent blotting, some mucilaginous substance is added, for example, dextrin or gum arabic. As the ink would be likely to mold on being exposed to the air, a small quantity of some fungicide, such as carbolic acid, is used to kill the germs that may fall into the ink from the air.

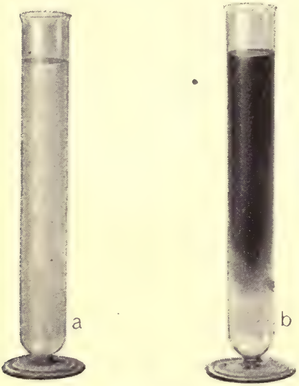


FIG. 93. — FERROUS TANNATE INK OXIDIZED BY AIR.

296. Logwood Inks. — Logwood, or campeachy wood, as it occurs in the market, consists of chips of the campeachy tree which grows in Mexico, Central America, and the West Indies. When boiled in water, a dye is extracted from logwood which has long been used to improve the quality of gall inks. Potassium chromate when added to logwood extract obtained in the manner just mentioned yields a black fluid; ferrous and copper salts yield dark colored fluids that oxidize more slowly than gall inks.

297. Nigrosin Inks. — Nigrosin is an aniline dye extensively employed for the preparation of cheap inks. Various grades of nigrosin are on the market, and for this reason nigrosin inks vary considerably. In some cases the coloring matter is not in solution and much of it settles as a thick mud in the inkwell. It is impossible to obtain good results by writing with a pen covered with this thick deposit. A good grade of nigrosin is soluble in water and yields a good ink for temporary use. The color is never black; it fades in a comparatively short time, and may be readily removed by washing in water or in a dilute solution of ammonium hydroxide.

298. India Inks. — Very pure, finely divided carbon, in the form of specially prepared lampblack, forms the basis of India inks. This is often made into small cakes by the use of some binder such as gum arabic or glue. When needed for use, a small portion of the cake is dissolved in water. There are also various fluid inks that contain finely divided carbon, held in suspension by a suitable vehicle. Such inks produce a permanent black and are not attacked by chemicals. Sometimes the ink is held to the paper by some adhesive material that deteriorates, so that in the course of time the pigment can be easily rubbed off. The only way in which spots of carbon ink can be removed is to make use of some liquid that will dissolve the binding material which holds the carbon to the paper or cloth. Carbon tetrachloride will in many instances do this.

299. Sepia is a pigment, varying from brown to black, secreted by several species of cephalopods, including the common cuttlefish. This pigment is discharged by the animal into the water, in order to darken it and make possible an escape from an enemy. The pigment of the cuttlefish was one of the early inks and is believed to have been used by the Romans. At the present time, the dried ink sacks of the cuttlefish are an article of commerce. The pigment is obtained by boiling the pulverized sacks with lye; neutralizing the lye with acid in order to precipitate the pigment; thoroughly washing the pigment with water and drying at a low temperature. The resulting material forms the base of the sepia used by artists.

300. Red Inks. — A great variety of red inks are offered for sale. The older varieties are ammoniacal solutions of the pigment of the cochineal insect, or an acetic acid solution of the dyestuff, Brazil-wood. The cochineal insect is a bug that lives on several species of cactus, one of which is cultivated for this purpose in Mexico, Central America, and several warm countries of the far east. The cochineal bugs of commerce are the dried remains of the female cochineal insect. After the females have deposited their eggs, they are killed by steam or hot water, or by spreading them on heated plates. Those prepared by the latter method are considered superior for use in making ink. Pure carmine is the pigment obtained from the cochineal insect and is soluble in water, but the name carmine has been given also to several colors derived from the pigment of cochineal.

Quite a variety of aniline colors, such as eosine and ponceau scarlet, form the base of most of the modern red inks. Water glass is used in the manufacture of waterproof red inks.

It is necessary to have some knowledge of the composition of a red ink in order to remove it from cloth. Some of the pigments used are very difficult to bleach. Carmine and eosine are readily destroyed by chlorine. *Chlorine should never be liberated in contact with silk or woolen goods.*

301. Copying Inks. — The demand for copying inks has greatly decreased since the introduction of the typewriter and carbon paper. When, however, it is desirable to retain a copy of a letter written with a pen, it is usually made by placing the original beneath the moistened page of a letter book and then, by means of a press, forcing the two firmly together. A portion of the ink enters the thin page of the letter book, and an exact copy of the letter is obtained. A good copying ink must not harden rapidly and should possess a considerable body. These qualities are secured by the addition of some slightly hygroscopic substance, such as sugar, dextrin, or glucose, to ordinary ink. Copying inks of excellent quality are on the market and are inexpensive.

302. Printers' Ink is usually a thick linseed oil varnish to which soap and finely divided carbon have been added. The varnish is obtained by heating linseed oil until the more volatile portions of the oil are driven off, and a thick liquid remains which can be drawn out in long filaments. The lampblack is then incorporated. Soap is added to the better grades of ink to prevent the type from adhering so firmly to the ink that the print will be smeared when the paper and type separate. In the cheaper grades of ink, long continued boiling is obviated by the addition of rosin, and linseed oil may be replaced by a less expensive material, such as rosin oil or nut oil.

SUMMARY

Black Writing Inks depend for their color upon one of the following: (*a*) the formation of ferric tannate, (*b*) an aniline dye, generally nigrosin, (*c*) finely divided carbon, usually in the form of lampblack.

The Tannic and Gallic Acids used in the manufacture of inks are obtained chiefly from nutgalls, which are morbid growths produced on the twigs of oak trees by gall-flies.

Iron Inks are water solutions of iron salts of tannic and gallic acids to which have been added (*a*) a dye to make the ink visible when first used, (*b*) a mucilaginous substance to cause the ink to better adhere to the pen, (*c*) a preservative to prevent the growth of fungi in the ink.

Iron Ink Spots may be removed from white cotton or linen goods by the following course of procedure: (*a*) the reduction of insoluble ferric tannate to soluble ferrous tannate, (*b*) washing in water, (*c*) bleaching the temporary color, (*d*) careful removal of the bleach.

Nigrosin Inks are water solutions of nigrosin. They are neither black nor permanent, and can be removed by washing.

India Inks depend upon finely divided carbon for their color. The carbon is held in suspension by a suitable vehicle which contains a binder to hold the carbon to the paper. Carbon is the most durable pigment used in the manufacture of ink. The permanence of an India ink depends upon the adhesive nature and the lasting qualities of the binder.

Sepia Inks are made from a pigment secreted by cuttlefish. They are among the most durable of inks.

Red Inks vary greatly in composition. The pigment used in making a red ink may be obtained from the cochineal insect or from Brazil-wood, or it may be one of the soluble synthetic dyes.

Copying Inks contain some slightly hygroscopic substance in addition to the materials used in making an ordinary ink.

Printers' Ink is a carbon ink and the vehicle is generally a linseed oil varnish.

The Removal of Ink Spots from colored cloth and from white silk and woolen goods without injury to the fabric is difficult and often impossible.

EXERCISES

1. Mention three classes of black writing inks.

2. What are some of the general properties of the tannins?

3. What is the chief source of the tannic and gallic acids used in the manufacture of ink?

4. What causes nutgalls to form?

5. What relation does tannic acid bear to gallic acid?

6. Briefly state the principles upon which the manufacture of an iron ink is based.

7. Why does a mild reducing agent such as milk aid in the removal of fresh spots of an iron ink from clothing?

8. Compare the properties of a nigrosin ink with those of an iron ink.

9. What is the pigment used in making India ink?

10. Upon what does the durability of India ink depend?

11. What are sepia inks? How do the colors of sepia inks compare with the color of a carbon ink?

12. Name some of the pigments used in the manufacture of red ink.

13. What is pure carmine? Of what do most of the carmines on the market consist?

14. Why is it generally more difficult to determine the course of procedure for the removal of red ink spots than for the removal of black ink spots from cotton goods?

15. How do copying inks differ from ordinary inks?

16. Briefly state the composition of a good quality of printers' ink.

CHAPTER XXVIII

TEXTILE MATERIALS

303. Plant and Animal Fibers. — Cotton, linen, wool, and silk are the materials from which the various fabrics used in the home are commonly woven. Cotton is the seed hairs of the cotton plant. Linen is made from the fiber of the flax plant, and to a less extent from hemp. Jute, the bast fibers of the jute plant, which grows chiefly in India and Ceylon, is employed to some extent as a cheap substitute for linen. The term wool, when used in a broad sense, refers to any animal hair which is sufficiently fine and long to be made into a thread that can be woven into cloth suitable for use as clothing. The term woolen goods includes not only the cloth made from the hair of the sheep, but alpaca, cashmere, and mohair, as well. Alpaca is made from the fine hair of the fleece of the llama. Cashmere is made from the wool of the Thibet goat. Mohair is woven from the fine hair of the Angora

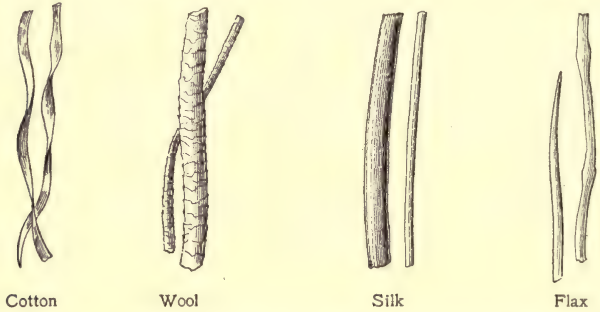


FIG. 94. — IMPORTANT TEXTILE FIBERS. (Highly Magnified.)

goat. Silk is manufactured from the thread spun by several species of caterpillars to form the cocoons in which they undergo their transformations into moths. Practically all silk is obtained from the cocoons of the silkworm.

The chief constituent of all vegetable fiber is *cellulose*, a compound that is of the greatest importance, not only on account of its extensive use in the textile industries, but on account of the enormous quantities employed in the manufacture of paper, and in the nitrocellulose industries (Chapter XX).

304. Cotton. — Raw cotton fiber contains about 91% of cellulose, the remaining 9% being chiefly water, together with small quantities of fatty and nitrogenous substances. A cotton seed-hair is a single plant cell, tubular in shape, which, during the growth of the plant, is filled with liquid protoplasm. As the seed ripens, the protoplasm disappears, the tube collapses, and the hair takes a twist in the form of a spiral. This latter structure is characteristic of cotton and aids in the spinning of a thread from the seed-hairs. There are several species of cotton; that known to the trade as Sea Island cotton produces the longest and finest seed-hairs, and commands the highest price.

305. Cellulose. — Very pure cellulose can be obtained from raw cotton by boiling it in an alkali, such as a solution of sodium carbonate, or a dilute solution of sodium hydroxide; rinsing first with water and then with a dilute solution of an acid; thoroughly washing and finally drying. From a chemical standpoint, cellulose possesses both weak acidic and weak basic properties. Neither acid nor basic dyes adhere to pure cotton fiber. The chemical nature of cellulose is utilized in making mercerized cotton and several varieties of artificial silk.

306. Mercerized Cotton was named for John Mercer who, in 1844, first published the principles of its manufacture. When cotton is treated with a concentrated solution of sodium hydroxide, it contracts to about three fourths of its original length, and is converted into a new substance called alkali cellulose. If the alkali cellulose is now

Copyright by Underwood & Underwood, N. Y.

FIG. 95. — PART OF THE 4,000,000 BALES OF THE YEARLY TEXAN COTTON CROP.

stretched to the length of the original cotton, and then thoroughly washed, it is changed to cellulose hydrate, and the fiber takes on a silky sheen. The best results are obtained when the sodium hydroxide solution contains from 27 % to 32 % of caustic soda, and is used at a temperature below 21° C. The luster is greatly affected by the tension which is applied simultaneously with, or just after, the formation of the alkali cellulose. Mercerized cotton is stronger than ordinary cotton and has a greater affinity for dyes.

307. Artificial Silks. — At least three classes of silks are made from cellulose, namely, pyroxylin silks, silks made from a solution of cellulose in ammoniacal cupric oxide, and those made from viscose.

308. Chardonnet Silk was named for Count Hilaire de Chardonnet who perfected a process for its manufacture. It is the best known of the pyroxylin silks.

In the manufacture of Chardonnet silk, pure cellulose is converted into collodion, which is forced through fine capillary tubes by a pressure of from 40 to 50 atmospheres. As soon as the fine threads of collodion come in contact with air, they solidify and can be rolled on bobbins. The fine threads are kept moist until after the formation of coarser threads suitable for weaving. The coarser threads are made by twisting together from 12 to 20 of the finer threads. Since pyroxylin is very inflammable, it is not suitable for use as clothing and must be converted into a substance much less easily ignited. This is brought about by treating the nitrocelluloses with some substance, for example, a solution of calcium sulphide, that will change the nitrocelluloses to cellulose, but will leave the cellulose in a form which closely resembles silk in appearance.

309. Pauly's Silk. — In making artificial silks of this class, the cellulose is either dissolved directly in a cuprammonium solution, or is converted into alkali cellulose and then dissolved.

310. Viscose Silk. — Viscose is made by treating cellulose, obtained chiefly from wood, with a sodium hydroxide solution and then adding carbon disulphide to the soda cellulose that is formed. It dissolves readily in water and the water solution decomposes when exposed to air, yielding cellulose as one of the products of decomposition. Viscose is so unstable that it cannot be stored and transported over long distances unless great care is taken to have the containers tight and to keep the temperature near the freezing point of water. Viscose, or rather viscoid, the precipitated cellulose obtained from it, has many uses. It is employed as sizing for paper and as a substitute for celluloid. It bids fair to become a very important substance for use in the manufacture of artificial silk, or luster cellulose.

The manufacture of viscose silk is carried on essentially as follows. A water solution of viscose is filtered to free it from particles of solid cellulose that would clog the fine capillary tubes of the spinning machine. The threads are then spun in the usual way, but after leaving the spinning tubes they are allowed to hang so as to be stretched by their own weight. The threads are then rapidly converted into cellulose by means of currents of warm air. In place of air, solutions of ammonium chloride and of ammonium sulphate are said to be used by some manufacturers to convert the viscose threads into cellulose. There are a great many mechanical difficulties to be overcome in making viscose threads fine enough for use as a substitute for silk. In spite of these difficulties a viscose product scarcely to be distinguished from silk is on the market. It has a more brilliant luster than silk, compares favorably with it in strength, and seems destined to enter into keen competition with the genuine article.

311. Linen consists of bast fibers, chiefly obtained from flax. Plants that are gathered before the seed has ripened yield a fiber most suitable for making linen thread. When especially fine fiber is desired, the plants are raised under conditions that cause them to have slender stems. Plants intended for the production of linen are pulled, roots and all, and have their leaves and seed-pods removed by a process called *rippling;* the residue is known as *straw.* The bast fibers are separated from the undesirable parts of the straw by one of the several methods termed *retting.* The natural means of retting consist of processes of decay, during which the bast fibers are thoroughly loosened. Chemical retting involves the use of dilute sulphuric or hydrochloric acid solutions and requires a much shorter time than the natural process. After the retting is complete, the flax is thoroughly washed, dried, and then submitted to mechanical processes that free the fibers from the woody tissue and make them into bundles of filaments ready for spinning.

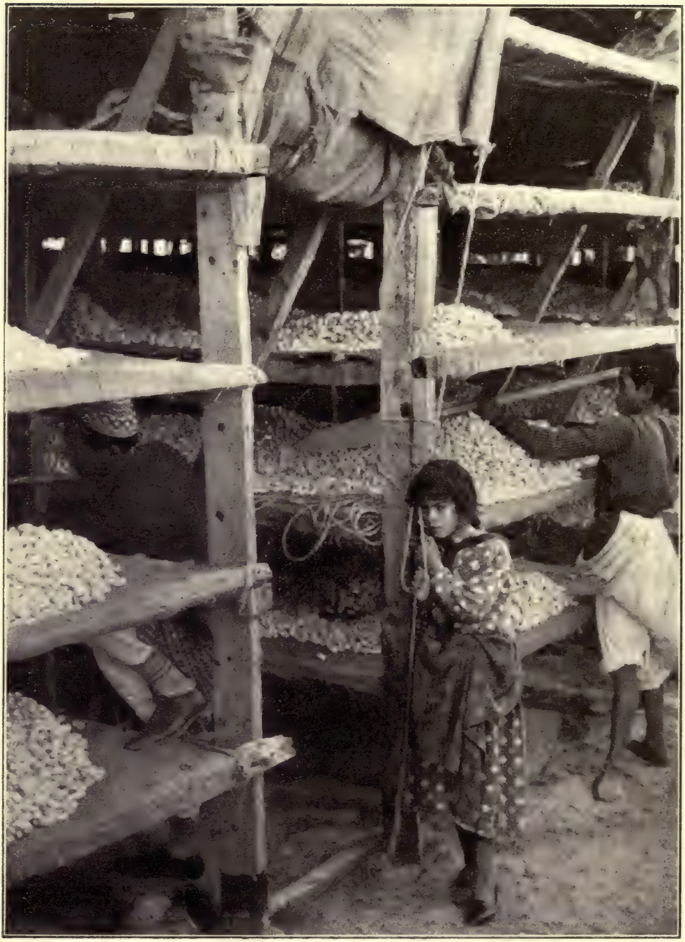
Linen is not pure cellulose, and is more readily disintegrated than cotton by strong alkalies and by chlorine and similar oxidizing agents. The differences between the shape of linen fiber and of cotton fiber as revealed under the microscope (Fig. 94), furnishes the most reliable method for distinguishing linen from cotton. Old linen that has been laundered many times is practically pure cellulose and cannot be distinguished from cotton by chemical tests.

312. Wool is composed of nitrogenous substances containing sulphur. Unwashed wool, in addition to dirt held mechanically to the fiber, contains incrusting matter that consists of two parts; one soluble in water (the *suint* or wool-perspiration), and the other soluble in fat solvents (the *yolk* or wool-fat). Either of the words "suint" or "yolk" is often used as the name for the complete incrusting material.

Preparatory to being made into yarn, wool is freed from dirt and the incrusting material. This may be accomplished by a single operation, or the process may be divided into two steps. The one-step process (*scouring*) is accomplished by washing the wool in a weakly alkaline solution of soap, or by the use of dilute solutions of such alkalies as ammonium carbonate, ammonium hydroxide, and sodium carbonate. The wash water in this case contains the wool-grease and also potassium salts, both of which are valuable substances. For this reason, the wash water is sometimes evaporated to dryness and then calcined for the purpose of securing the potassium in the form of potassium carbonate. At other times, the suspended impurities are allowed to settle and then sulphuric acid is added to the warm solution to decompose the soaps and to cause the oils and fats to rise to the surface. *Lanolin*, much used as a basis for salves and ointments, is a purified wool-fat. The wool-grease and suint are also obtained separately by making use of the fact that the wool-grease is soluble in fat solvents (benzine, petroleum, naphtha, ether, etc.) while suint is soluble in water.

Wool is readily attacked by alkalies, even dilute solutions of sodium hydroxide causing it to dissolve. In this respect, it is in marked contrast to cotton. On the other hand, acids affect cotton much more readily than they do wool. Dilute solutions of the mineral acids have practically no effect on wool. Practical use is made of this fact by employing solutions of sulphuric acid and of aluminum chloride to free wool from burs and other vegetable matter that have become entangled in it. When heated in the presence of water, the aluminum chloride reacts with the water, yielding hydrochloric acid, which attacks the vegetable fiber so that it falls to pieces and can be washed from the wool. Concentrated mineral acids destroy wool fiber. Wool is rather sensitive to heat; when raised to 100° C., the fiber rapidly becomes brittle. Strong oxidizing agents, such as chlorine, attack wool. Since wool is very hygroscopic, this fact should be taken into consideration when purchasing it.

313. Silk is a nitrogenous substance containing no sulphur, differing in this respect from wool. The preparation of silk thread involves several operations, the more important of which will be referred to briefly. The cocoons (§ 303) are soaked in warm water for the purpose of softening the silk-glue so that the fiber may be reeled. During the process of reeling, two threads (composed of from 4 to 10 fibers) are made to cross so that their rubbing against each other softens the silk-glue and causes the fibers to adhere in the form of solid uniform threads of *raw silk*. Raw silk is so hygroscopic that it will absorb moisture amounting to 30 % of its weight and yet appear to be dry. This makes it desirable, for the purpose of trade, to determine accurately the amount of water contained in a lot of silk to be purchased. The operation of determining the amount of moisture held by a textile



Copyright by Underwood & Underwood, N. Y.

FIG. 96. — DRYING SILKWORM COCOONS IN TURKEY.

fiber is termed *conditioning;* thus we speak of silk-conditioning, and of wool-conditioning.

Raw silk has a harsh feel and is lacking in luster, so, before being made into cloth, it is subjected to treatment that makes it soft and glossy. This consists in suspending the silk in a warm soap solution to dissolve at least a part of the silk-glue, rinsing in a sodium carbonate solution, and then wringing. Two or three soap baths are used for the finest quality of silk. Hanks of this are tied in several places, put into linen bags, and boiled in a soap solution until all of the silk-glue has been removed. Such a silk has about 70% of the weight of the raw silk from which it was made. *Ecru silk* is obtained by treating raw silk with a weak soap solution until from 2% to 5% of the weight of the raw silk has been removed, then washing it and frequently bleaching it with sulphur dioxide. Dilute solutions of acetic and tannic acids when dried on silk increase its luster and cause it to rustle when rubbed. During the process of dyeing, silk is frequently *weighted*, that is, mordanted with iron or tin salts which form deposits on the fiber, so that the weight of the goods is often doubled. Weighted silks are likely to crack.

Silk is more resistant than wool to the action of alkalies, and less resistant than cotton. Concentrated hydrochloric acid rapidly dissolves silk, which differs in this respect from wool. Oxidizing agents, such as chlorine and hypochlorites, attack the fiber of silk.

314. Bleaching. — The differences in the chemical composition of the various textile fibers and of the coloring materials to be destroyed, make it impossible to use a single method for bleaching cotton, linen, wool, and silk. Cellulose is capable of withstanding the action of chlorine as well as that of acid and of alkaline baths. On the other hand, wool and silk are readily destroyed by both chlorine and alkalies.

315. Bleaching of Cotton. — Oxygen, derived from hypochlorous acid, and by the action of chlorine on water in the presence of organic matter, is practically the only substance used for bleaching cotton. The hypochlorous acid and chlorine are obtained by the reaction between acids and bleaching-powder, a substance made by passing chlorine over slaked lime. Preparatory to bleaching, cotton yarn is *boiled out* in alkaline solution to remove the waxy coating from the fiber. This process consists in causing a hot alkaline solution to circulate through the yarn in a closed tank, called a *kier*. After being boiled out, the yarn in the kier is thoroughly washed, then taken out and treated with a cold, dilute solution of bleaching-powder (*chemic*). The yarn is next washed and *soured*, that is, treated with a dilute solution of sulphuric or of hydrochloric acid, or, after the washing, it may be exposed for some time to the carbon dioxide of the air. The acids in general, even as weak a one as carbonic acid, react with the bleaching-powder retained by the cotton fiber, producing hypochlorous acid and free chlorine. The hypochlorous acid is itself an oxidizing agent, and the chlorine liberates oxygen from the water in the fiber. This oxygen destroys the coloring matter of the yarn. After being bleached, the yarn is thoroughly washed, worked in a soap solution, and then dried. In the cases of raw cotton fiber and cloth, the process varies considerably from that described above, but the principles involved are the same.

316. Bleaching of Linen. — As unbleached linen fiber is not pure cellulose, and is much more readily attacked by chlorine than cotton, a different process of bleaching is employed. The bleaching of linen is one of the ancient industries, and the old method is still practiced to a limited extent. This consists of steeping the material to be bleached in an alkaline solution, exposing it out of doors on the grass, meanwhile sprinkling it from time to time with water. It is then dipped in buttermilk and washed with soap and water. All of this is a tedious process, often requiring several months for its completion. Shorter processes involving the use of alkalies, chloride of lime, acids, and exposure on grass, have been invented, but great care must be exercised not to unduly weaken the fiber by chlorine.

317. Bleaching of Wool is usually accomplished through the agency of either sulphurous acid or sodium peroxide. When sulphurous acid is employed, the wool is thoroughly scoured, washed, and then subjected to the action of sulphur dioxide produced by the burning of sulphur. After being bleached, the wool is rinsed in water containing a little bluing. A bath of sodium bisulphite, followed by one of dilute sulphuric acid, is also used to produce sulphurous acid in contact with the fiber.

When sodium peroxide is sprinkled into a bath of dilute sulphuric acid, hydrogen peroxide is produced. This readily decomposes, when in contact with organic substances, yielding oxygen. Since strong alkalies rapidly destroy wool, it is essential not to add an excess of sodium peroxide, but, as the bleaching proceeds much more rapidly in the presence of alkalies, the bleaching bath is generally made slightly alkaline by the use of some weak alkali, for example, borax.

318. Bleaching of Silk. — Silk is sufficiently light colored to be used unbleached for most purposes. When it is desirable to destroy the light yellow shade of the natural article, sulphurous acid, or sodium peroxide, may be used as in the case of wool. A cold dilute solution of a mixture of nitric and hydrochloric acids is also employed to bleach silk.

SUMMARY

Cotton is nearly pure cellulose.

Cellulose is not readily attacked by dilute acids and alkalies, nor by oxidizing agents such as chlorine. It is converted into the nitrocelluloses by mixtures of concentrated nitric and sulphuric acids.

Artificial Silks consist of cellulose. During their preparation, the raw material is treated by various processes which impart to the finished product a silky sheen.

Linen is made from the bast fibers of several plants, the flax plant being its chief source. It is not as pure cellulose as cotton, and is much more readily disintegrated by strong alkalies and by chlorine. The microscopical examination of the structure of the fiber furnishes the most reliable means of distinguishing between cotton and linen (Fig. 90).

Wool is composed of nitrogenous substances containing sulphur. It readily dissolves in hot solutions of alkalies, and is colored by many dyes that do not affect cotton, for example, picric acid.

Silk is a nitrogenous substance containing no sulphur. It is more resistant than wool and less resistant than cotton to the action of alkalies. Concentrated hydrochloric acid rapidly dissolves silk.

EXERCISES

1. What percentage of raw cotton is cellulose?
2. How may pure cellulose be obtained from cotton?
3. How is mercerized cotton made?

4. Why would it be desirable to substitute the name "luster cellulose" for "artificial silk"?

5. Briefly describe a process for making artificial silk.

6. From the bast fibers of what plant is linen chiefly obtained?

7. Compare the microscopical structure of linen with that of cotton.

8. Why is it much more difficult to distinguish by chemical reactions between cotton and linen that has been laundered many times than it is to distinguish between cotton and unbleached linen?

9. Why is it difficult to bleach linen without injury to the fiber?

10. Mention two valuable by-products obtained during the preparation of wool for weaving.

11. What practical application is made of the fact that hydrochloric acid attacks vegetable matter much more readily than it does wool?

12. Explain why soap containing a considerable quantity of free alkali should not be used in washing woolen goods.

13. How could a person determine by a chemical test whether a piece of goods was pure wool or a mixture of wool and cotton?

14. Why should not woolen goods be left on a steam radiator?

15. How does wool differ from silk in chemical composition?

16. Tell how to distinguish between silk and artificial silk.

17. Why should bleaching powder never be used to remove a stain from silk?

18. What is the principal compound used in the bleaching of cotton?

19. What are the bleaching agents employed for wool and silk?

CHAPTER XXIX

DYES AND DYEING

319. Modern Dyes. — Each year the number of persons engaged in using their own handiwork to make their homes and clothing more artistic is increasing. Dyes, intelligently selected and artistically used, furnish a valuable and inexpensive means of increasing the pleasing appearance of the home. Modern methods of dyeing date from the discovery of mauve by Perkin in 1856. Since that time the discoveries of other dyestuffs have followed in rapid succession, and the methods of dyeing have been greatly simplified. Pleasing shades, that neither fade when exposed to the action of sunlight nor are removed during the process of washing with water and a good soap, can be obtained on small quantities of cotton, linen, silk, wool, or mixed goods. The chemistry involved in the synthetic preparation of dyes is complex, and the chemical names and formulas of the compounds used would mean nothing to the student of elementary chemistry. Dyes may, however, be classified so that those placed in one group will be suitable for use in coloring certain textiles. A dye may give excellent results when used with wool and be worthless for use with cotton.

320. Direct Dyes for Cotton. — A few years ago it was thought to be impossible to dye cotton and linen without the use of some substance, called a mordant, that would hold the color to the fiber. Recently quite a number of dyes have been discovered that adhere to cotton and linen, and some of them possess a satisfactory permanence. A dealer in dyes is likely to assign a characteristic name of his own to a special class of dyes, so we find such names as Dianil, Diamine, Naphthamine, and Benzo used by different firms to indicate direct dyes for cotton. These terms take the part of a family name, and the color that of the given name. Dianil Yellow, Dianil Fast Blue, Dianil Fast Black; Naphthamine Fast Yellow, Naphthamine Fast Blue, and Naphthamine Direct Black are direct yellow, blue, and black dyes for cotton. Dyes of this class are not only used to color vegetable fibers, of which cotton, linen, and paper goods are made, but some of them are of great value for the dyeing of silk, wool, and mixed goods as well. The list of direct dyes is being increased rapidly, so that it will soon be possible to obtain by their use fast colors of almost any shade.

321. Use of Direct Dyes. — The application of direct dyes is so simple that little experience is necessary for obtaining a uniform, satisfactory color. The preparation of the dye bath consists in dissolving the dye in a little hot water, straining the concentrated solution through fine muslin, to remove any particles that may remain undissolved, and then adding the solution to the quantity of water required for the bath. In order to increase the amount of color that may be obtained from the bath, some sodium salt, such as common salt, sodium sulphate, or sodium phosphate, is frequently added to the bath to lessen the solubility of the dye. For obtaining a uniform shade, it is essential that the goods be thoroughly wet with water before being placed in the bath, and that they be kept in motion while in the dye bath, so as to expose every part of the goods to the dye for the same length of time. The bath should be hot before the goods are placed in it, and should be rapidly brought to the boiling point after the goods are added, and kept boiling until the desired shade is obtained. After being taken from the bath, the goods should be thoroughly rinsed with water and then dried. Neither washing soda, strongly alkaline soap, nor bleaching powder should be used in washing goods whose color depends upon direct dyes.

322. Direct Developed Dyes. — An interesting process for obtaining certain colors on cotton goods consists in applying a direct dye, and then placing the colored material in a very dilute bath of sodium nitrite and hydrochloric acid. After rinsing, the goods are placed in a bath containing a chemical that will cause a color entirely different from the original to appear on the goods.

323. Acid Dyes. — Dyes belonging to this class of colors are sold in the form of the potassium, ammonium, and calcium salts of the color acids. From one of these salts the color acid is liberated in the dye bath by the addition of an acid, either sulphuric, acetic, oxalic, or formic acid being commonly employed for this purpose.

This class of dyes is seldom used for coloring cotton, but is of great value in dyeing animal fibers, which in general possess sufficient basic properties to cause them to combine with the free color acid. Free alkalies quickly remove acid colors from the fiber. For this reason, the goods dyed with acid dyes fade rapidly when washed with laundry soap or washing powder. The acid colors are, as a class, extremely fast when exposed to light. The properties just mentioned make acid dyes of special value for coloring wool, silk, leather, and feathers when the articles made from them are not intended to be washed. Fast Acid Blue, Palatine Scarlet, Acid Yellow, Cashmere Black, and Nero Cyanine Blue are examples of acid colors.

324. Basic Dyes. — Fuchsine, methyl violet, methylene blue, Bismarck brown, and malachite green are among the common basic colors. Members of this class of dyes readily form salts with acids. They dye silk and wool directly, because these substances possess acid as well as basic properties. In order to have a basic dye adhere to cotton or to linen, it is necessary to first treat the fiber with some substance, a *mordant* (from the Latin *mordeo*, to bite), that will cling to the goods and also to the color. The mordant serves as a bond of union between the dye and the fiber to be colored. It fixes the dye so that it cannot be washed from the goods. Cellulose fibers are treated with an acid mordant before being colored by basic dyes. Tannic acid is commonly used for this purpose, and is fixed on the fiber by treatment with a solution of tartar emetic before the goods are placed in the dye bath. The process of mordanting greatly increases the difficulty of obtaining an even shade, as considerable skill is required to mordant the goods uniformly. Straw, raffia, willow, and bark-tanned leather generally contain sufficient tannic acid to fix basic dyes. These colors may also be used as direct dyes for artificial silks made from nitrocellulose.

As a class, basic dyes fade rapidly when exposed to light. They are too gaudy to be generally pleasing to persons of refinement, but this defect can be readily overcome by adding to the dye bath a small quantity of a complementary color. In fact, very interesting results may be obtained by mixing dyes of different colors.

325. The Sulphur Colors are prepared by the action of sodium sulphide on various organic substances. When goods dyed with them are exposed to the air, pleasing shades are produced that do not fade and are not removed by washing. Since the sulphur dyes are used in strongly alkaline baths, and because hot alkalies readily attack wool and silk, these colors are chiefly used with cotton and linen goods. Only one dye bath is necessary, the color being fixed by exposure to the air. The sulphur colors appear on the market under the class names of Thyogene, Kyrogene, Thion, Pyrogene, and Kaligene.

326. The Vat Colors. — Indigo, which is produced by plants belonging to the genus Indigofera, was the original dye of this class, and has been employed for many centuries. One of the greatest triumphs of modern science was accomplished when chemists prepared indigo artificially, at a cost which enabled the synthetic product to compete with the natural article, and so simplified the method for its application that it could be used conveniently in the home. These discoveries followed the scientific determination of the chemical constitution of indigo, and of chemical changes that took place in the dye bath.

Indigo occurs in the form of an insoluble substance that can be rendered soluble through the agency of reducing agents. The soluble material enters the fiber, and on exposure to the air becomes converted by oxidation into the insoluble color compound. At the present time, large color manufacturers place the reduced indigo on the market in a form which is readily soluble in an alkaline bath in the presence of a small quantity of a reducing agent. The goods are placed in a vat, containing the reduced coloring matter in solution, and stirred until they become thoroughly saturated. They are then passed through a wringer several times, in order to leave the dye evenly distributed, and hung so as to expose them to the oxidizing action of the air. The bath is used either cold or lukewarm, so that the alkali does not injure wool as much as it would if hot. After the color has developed, the goods are carefully washed to remove the alkali, and then boiled in a soap bath to remove the excess of dye.

Recently, dyes which are applied in a manner similar to indigo, producing colors other than blue, have been placed on the market. These colors are known as vat dyes and appear under the class names Helindrone, Algol, Indathrene, Hydrone, and Ciba. As a class, vat dyes furnish the most satisfactory fast colors yet introduced.

327. Other Classes of Dyes. — Classes of dyes other than those mentioned, such as the mineral dyes, iron buff, chrome yellow, and Prussian blue, and the alizarine dye, Turkey red, have been omitted, as they are far more difficult to apply than those described.

328. Synthetic Dyes compared with Vegetable Colors. — The basic dyes are, in general, made from aniline and constitute the true aniline colors. It is unfortunate that this term has been popularly extended to include all dyes prepared artificially. Basic dyes were the first colors to be synthesized. On account of the rapidity with which they change color when exposed to light, the opinion arose that all synthetic colors faded much more rapidly than vegetable dyes. This is far from true; in fact, the fastest colors produced in any age are found among the modern synthetic dyes, and their range of color far exceeds that known to the ancients.

SUMMARY

Direct Dyes produce reasonably fast colors on textiles without the aid of mordants. There has been a great increase in the number of direct dyes for cotton and they are rapidly replacing the basic dyes. Cotton colored by a direct dye should not be washed in alkaline solutions.

Acid Dyes are of great value for coloring animal fibers. They are fast to light but are readily removed by alkalies.

Basic Dyes cannot be used for coloring cotton without the aid of a mordant, though they are direct dyes for silk and wool. They are not fast to light and yield gaudy colors.

Sulphur Colors are especially adapted for the dyeing of cotton and linen. They produce pleasing shades, fast to light and not removable by washing.

Vat Colors are rendered soluble by reducing agents and the color is developed on the goods by the oxidizing action of the air. The best known vat color is indigo, an ancient and highly esteemed dye.

EXERCISES

1. Why is it desirable to increase the number of dyes that can be conveniently used to produce fast colors on small quantities of material?

2. What are some of the advantages to be derived from the use of direct dyes?

3. Is a direct dye for wool always a direct dye for cotton?

4. Why is a sodium salt generally added to a dye bath containing a direct dye for cotton?

5. Why should the material to be colored be thoroughly wet with water before being placed in the dye bath?

6. Why is it essential to work goods constantly while they are in the dye bath?

7. What is the meaning of "direct developed dye"?

8. For coloring what classes of textiles are acid dyes chiefly used? Why?

9. What are some of the advantages and some of the disadvantages to be derived from the use of acid dyes?

10. Why is it necessary to mordant cotton goods that are to be colored by basic dyes?

11. To what textiles are the sulphur colors best suited ?

12. What may be said concerning the permanency of the sulphur colors ?

13. What is meant by a "vat color" ?

14. Why are the mineral dyes and alizarine less used than formerly ?

15. How did the incorrect impression arise that all artificial dyes are less fast to light than the vegetable colors ?

CHAPTER XXX

PHOTOGRAPHY

329. Chemical Changes produced by Light. — While we are familiar with the fact that light is frequently produced in chemical action, we often fail to realize that the converse is true. Many chemical actions are induced by light, and some proceed only when energy can be absorbed in the form of light. The fading of many dyes is a common example of this fact. The building of starch from carbon dioxide and water in the leaves of plants occurs only under the influence of sunlight, which supplies the necessary energy. This may perhaps be considered the most important of all chemical actions, since all life depends upon it. Several of the chemical changes produced by light are used as the basis of photographic processes.

330. Blue Prints. — A comparatively simple process is that employed to produce blue prints, much used to make copies of architect's plans and engineer's drawings, and occasionally for photographs. It depends on two simple chemical facts, which are:

(1) that ferric salts are changed to ferrous salts by light if a reducing agent is present;

(2) that potassium ferricyanide reacts with ferrous salts, producing an intensely blue substance, Turnbull's blue. We may write equations for these reactions as follows:

$$\underset{\substack{\text{ferric}\\ \text{chloride}}}{2\,\mathrm{FeCl_3}} + \underset{\substack{\text{oxalic acid}\\ \text{(reducing agent)}}}{\mathrm{H_2C_2O_4}} \longrightarrow \underset{\substack{\text{ferrous}\\ \text{chloride}}}{2\,\mathrm{FeCl_2}} + \underset{\substack{\text{hydrochloric}\\ \text{acid}}}{2\,\mathrm{HCl}} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{2\,\mathrm{CO_2}}$$

$$\underset{\substack{\text{ferrous}\\ \text{chloride}}}{3\,\mathrm{FeCl_2}} + \underset{\substack{\text{potassium}\\ \text{ferricyanide}}}{2\,\mathrm{K_3Fe(CN)_6}} \longrightarrow \underset{\substack{\text{Turnbull's}\\ \text{blue}}}{\mathrm{Fe_3[Fe(CN)_6]_2}} + \underset{\substack{\text{potassium}\\ \text{chloride}}}{6\,\mathrm{KCl}}$$

Paper on which blue prints are to be made is coated with a mixture that will allow both of these actions to occur simultaneously. The mixture contains ammonium ferric citrate, which serves the double purpose of furnishing the iron compound and the reducing material, which, in this case, is the citrate radical of the salt. The other constituent is potassium ferricyanide. Where light strikes such paper it changes color, and on washing, a pronounced blue color is produced. At the same time, unchanged material is washed away.

331. Terms used in Photographic Processes. — For the complete photographic process four classes of substances are nearly always employed. They are:

(*a*) the sensitive substance;

(*b*) the sensitizer, which makes the action of the light on the sensitive substance more pronounced, and which does this by combining with one of the products produced by the action of light;

(*c*) the developer, which brings out or exaggerates the initial action of light;

(*d*) the fixer, which removes substances not altered by the preceding operations, and which makes the plate or print inactive to further influence by light, and therefore permanent.

In blue prints, the ferric salt is the sensitive substance, the citrate radical is the sensitizer, the potassium ferricyanide is the developer, and water is the fixer.

332. Silver Plates. — The great proportion of all photographic operations makes use of the fact that silver bromide is sensitive to light. The nature of the change that takes place is not well known, but it results in the liberation of an amount of bromine which is exceedingly small, even after a long period of exposure. By mixing the silver bromide with gelatin, a much more sensitive combination is obtained, because gelatin is a strong absorbent of bromine, and therefore aids the liberation of bromine from the silver bromide. In this way, it acts as a sensitizer for silver bromide. In preparing plates for use in cameras the emulsion of silver bromide in gelatin is spread in a thin layer on sheets of glass or on transparent celluloid. These are exposed to the image that is formed in the camera, and the sensitive film is affected in varying degrees by the spots of light and shade. When removed from the camera, these plates show no change to the eye. But when they are put in an alkaline solution of a weak reduc-

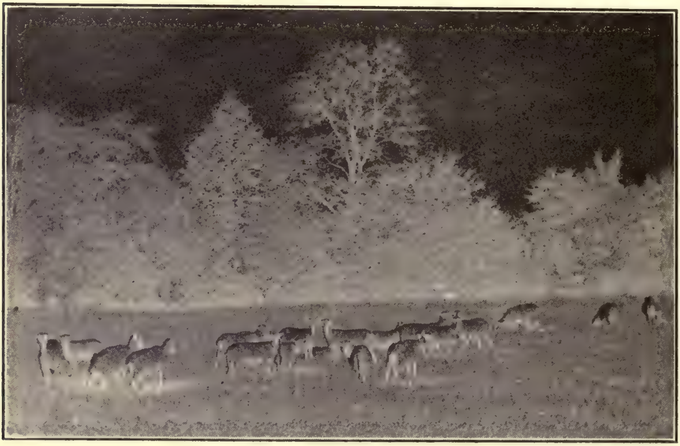


FIG. 97 A. — THE PLATE OR NEGATIVE.

ing agent, the effect of the light soon becomes apparent. Black spots appear where most light struck the plate, and a *negative* picture is obtained (Fig. 97A). The explanation of the changes is as follows. It is supposed that the effect of the momentary exposure which forms the initial, invisible, so-called *latent* image, is to deposit an infinitesimal amount of silver.

FIG. 97 B. — THE PRINT OR POSITIVE.

$$\underset{\text{silver bromide}}{AgBr} \longrightarrow \underset{\text{silver}}{Ag} + \underset{\text{bromine}}{Br}$$

The solution of weak reducing agent which *develops* the plate acts most rapidly on those spots where the minute quantity of silver has been deposited, the silver acting as a catalytic agent. The action must be stopped at the point where a clear image is obtained, otherwise the entire amount of silver bromide would be reduced, and an entirely black plate obtained.

$$\underset{\substack{\text{silver}\\\text{bromide}}}{AgBr} + \underset{\substack{\text{hydrogen}\\\text{(any reducing agent)}}}{H} \longrightarrow \underset{\text{silver}}{Ag} + \underset{\substack{\text{hydrobromic}\\\text{acid}}}{HBr}$$

A considerable number of different substances are used as developers for silver plates. The more common ones are amidol, eikonogen, pyrogallic acid, ortol, etc. These are all complicated organic compounds. They are used in alkaline solution in order that the hydrobromic acid that is formed in the developing action shall be neutralized.

To fix a silver plate it is only necessary to dissolve out the silver bromide that has not been acted upon by the developer. A suitable solvent is found in sodium thiosulphate, $Na_2S_2O_3$, ordinarily called "hypo." Finally, thorough washing and drying complete the process, and a permanent negative is obtained.

333. Prints. — From one negative it is possible to obtain an indefinite number of positive prints (Fig. 97B). The processes are essentially the same as in making the negative. The sensitive substance is silver bromide, made more sensitive by some substance such as gelatin, or albumen, which also serves the purposes of holding the bromide to the paper and of giving surface texture to the paper. In the varieties of paper most used nowadays, only a latent image is formed during the exposure under the negative, and this is brought out by the reducing action of the developer, as with the negative. Fixing is accomplished with a solution of "hypo." Other types of paper, less used than formerly, are covered with a mixture that contains a developing agent as well as the sensitive mixture. Such papers show an image forming visibly during the exposure under the negative. These papers, after fixing, have an undesirable color, and require *toning*. This process is one of simple replacement. The print is immersed in a solution of gold chloride or of a platinum salt, and the metallic silver is replaced by metallic gold or platinum.

$$\underset{\text{silver}}{3\,Ag} + \underset{\text{gold chloride}}{AuCl_3} \longrightarrow \underset{\text{gold}}{Au} + \underset{\text{silver chloride}}{3\,AgCl}$$

Toning also makes prints more permanent.

334. Actinic Power. — Different colors affect silver bromide in unequal degree. Blue light has a very pronounced effect, while red and orange have almost none. It is because of this fact that we develop plates in red or orange light. Also, it is well known that red objects appear black in a photograph, and that blue appears white. Light which does not affect the plate is called *non-actinic.*

Since all colors do not have the same actinic power, ordinary photographs do not have true color values. To remedy this defect it is necessary to interpose color screens between the object and the plate, thus reducing the intensity of the more actinic colors, or to employ a special variety of plates called *orthochromatic.* These are like ordinary plates except that they have been treated with baths of certain dyes. In some manner not fully understood, these dyes have the power of increasing the sensitiveness of silver bromide for light of their own color. Photographs on this kind of plate are much more accurate in their representation of light and shade, but these plates have the disadvantage of being slower than the ordinary variety.

335. Color Photography. — Experimenters have endeavored for many years to perfect a process by which the colors of nature could be obtained in a photograph. The problem has been one of physics rather than chemistry, and in the more or less successful methods that have appeared, the chemical actions employed do not differ materially from those that have been described.

In one of these processes, the glass plate is covered with an extremely thin layer of starch *cells*, some of which have been stained red, others green, and still others violet. These are present in such proportion that the mixture appears white to the eye. The cells are compressed under heavy pressure until the plate is covered with a very thin transparent layer, which, under the microscope, would appear to be made up of dots of red, green, and violet. On this layer, an orthochromatic emulsion of gelatin and silver bromide is spread. The exposure in the camera is made with the glass side of the plate to the front, so that the layer of stained starch cells is between the image and the silver bromide film.

Since each colored starch cell can transmit only its own color of light, it is apparent that the silver bromide behind each red cell will be affected only by the red in that part of the picture. A similar thing is true for cells of each of the other two colors. When the plate is developed, therefore, a certain amount of opaque metallic silver will be deposited behind those red cells where red light fell in the image, behind the green cells where green light fell, and behind violet cells where violet light fell. But this is just the reverse of the condition that we desire; we want these spots to be transparent, so that red light will *come through* in the red parts of the picture.

Hence, after the plate has been developed and before it has been fixed, the metallic silver must be dissolved out, and the plate then returned to the developing bath so that the unchanged silver bromide will be turned into opaque metallic silver. The effect of this is to make the silver deposit positive instead of negative, and the plate will now be opaque in all spots except where red light passed through red cells, green light through green cells, and violet light through violet cells. In these spots the plate will be transparent, and the eye looking at it by transmitted light, will fuse the minute spots of color, and see a picture that approximates closely to the beauty of nature.

By this process only one picture can be obtained from each exposure in the camera, and the plate must be viewed by transmitted light.

SUMMARY

Light induces some chemical changes just as others are induced by heat.

Light-sensitive Substances are not uncommon. Important ones are silver compounds, especially *silver bromide*, and ferric salts. Silver compounds are used in ordinary photography, ferric salts in blue prints.

A Sensitizer is a substance used to increase the rapidity of the action of light. In ordinary plates, gelatin serves two purposes. It is a sensitizer, and it holds the silver bromide to the plate. It acts by absorbing bromine, one of the products of the action of light.

A Developer is used to bring out the effect of the light on the plate. In ordinary photography, this initial effect is not visible to the eye. For silver bromide plates, the developer is an alkaline solution of a weak reducing agent.

A Fixer is a substance used to dissolve sensitive material that has not been affected by the processes of exposure and development. It makes the plate permanent.

Negatives are pictures made in the camera. They have the light and dark of the object reversed.

Prints are made by practically the same chemical processes as those used to produce negatives.

Toning is sometimes used to obtain more pleasant colors than those that appear in the untoned print.

Ordinary photographs do not give correct representations of light and shade, warm colors appearing too dark and the cold ones too light. *Orthochromatic* plates and color screens partly correct this defect.

Plates that show photographs in color have been made by producing minute spots of red, green, and violet on a plate under the gelatin-silver bromide emulsion, and causing the various photographic operations to blot out by deposits of metallic silver those spots which should not appear in the picture. In this way pictures are obtained showing vividly all the colors of nature.

EXERCISES

1. What happens in the photosynthesis of starch in the leaves of plants?

2. Name some chemical actions that are caused by light.

3. What is the sensitive substance in blue-print paper? What sort of substance is needed as a sensitizer? Why is blue-print paper both developed and fixed by simple washing?

4. Why is not blue-print paper more commonly used in producing photographs?

5. What is the effect of light on silver bromide? How can the action be made more rapid? Explain this effect.

6. What is the chemical nature of the developers used for silver bromide plates? Why should the developing solution be alkaline?

7. Why are the darks and lights of the object reversed in a plate that has been exposed in a camera?

8. What is the dark substance in a photographic negative?

9. Why is gelatin used in making photographic plates?

10. Why do black spots appear on the hands when silver compounds have been handled in the laboratory?

11. Why can plates be exposed to red or orange light in the dark room during the operation of development?

12. Is the silver deposit that is finally left on a color-photography plate in the nature of a positive or a negative? Explain.

13. Why can only one copy of a color photograph be obtained?

CHAPTER XXXI

PAINTS, OILS, AND PIGMENTS

336. Purposes served by Paints. — The use of paints finds its origin in two widely different human necessities. Historically the more important of these is the need of surface decoration which is displayed by even the most primitive of savages. Civilization has developed this need into the various arts of design and pictorial representation. The other use arises from the fact that many materials used in manufacturing or building operations are subject to rust or decay. Paint delays this destructive tendency.

337. Nature of Paints. — Paints always contain an opaque solid and a liquid which holds the solid in suspension while the paint is being spread on a surface and which causes it to adhere firmly to the substance that it covers. The solid is called the *pigment*, and the liquid the *vehicle.* Pigments include many substances, from those that give the fundamental white through those that furnish all the wide range of color that we use. Vehicles are mainly of two classes: (*a*) oils that become solid, gum-like substances by absorbing oxygen from the air, (*b*) water that contains adhesive or cement-forming material.

The choice of pigment and vehicle depends entirely on the use which the paint is to serve. If it is to cover an outside surface, exposed to rain and weather, the highest possible degree of insolubility and chemical resistance to air, light, and water is desirable, in both pigment and vehicle. If, on the other hand, it is for inside work, such as covering plaster walls, or the canvas of stage scenery, glue and water make a satisfactory and cheap vehicle.

WHITE PIGMENTS

In white pigments the important qualities are:

(*a*) high covering power, tested by ascertaining how much black surface a given weight or a given volume will cover;

(*b*) durability;

(*c*) ability to combine well with linseed oil;

(*d*) pure whiteness of color as opposed to gray or yellow tinges;

(*e*) ease of application with the brush.

338. White Lead. — Until fifty or sixty years ago the only white pigment in use was white lead. This substance is a basic carbonate which we may describe as a mixture of lead hydroxide and lead carbonate, represented by the formula $Pb(OH)_2 \cdot 2\,PbCO_3$. This contains 31 % of lead hydroxide and 69 % of lead carbonate. The lead hydroxide appears to react with linseed oil, which is most frequently used as a vehicle, forming a smooth, easily worked substance. A high per cent of the hydroxide is desirable.

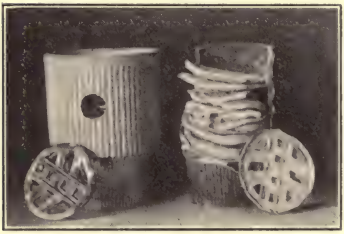


FIG. 98.

The oldest process for making white lead is known as the Dutch process. It is still used and more white lead is produced by it than by all other processes combined. Lead disks are placed in earthen pots that contain a little dilute acetic acid (Fig. 98); the pots, many in number, are piled in tiers, and embedded in tan bark, in such a way that a draft of air continually flows over them. The tan bark ferments, producing carbon dioxide and causing an elevation of temperature. After some 90 days, the action is completed. The long period of the action is the chief objection to the process, and is a reason for the search for other methods. Several of these are in operation. One of them hastens the action by using lead that is in a finely divided or "atomized" condition. In another, electrolysis is employed; but none of them have as yet succeeded in displacing the old process.

339. Sublimed White Lead. — This is a valuable white pigment that has come into use in recent years. It is obtained by the direct heating of galena (lead sulphide, PbS), and consists approximately of 75 % lead sulphate, 20 % lead oxide, and 5 % zinc oxide. It is more durable than white lead when exposed to sea air. When mixed with linseed oil it hardens (dries) rapidly, and forms a tough, impervious coating.

Other zinc-containing lead whites may contain zinc oxide up to 50 %. One of these, known as "standard zinc white," is made by mixing galena and zinc sulphide ores and obtaining from them a volatile product at a high temperature. This consists mainly of zinc oxide and lead sulphate. The heat causes a union between the lead sulphate and zinc oxide that could not be obtained by mechanical means.

340. Zinc Oxide is a pigment which is rapidly advancing into favor, particularly when mixed with other substances. A combination of white lead and zinc oxide, for example, gives a paint that is satisfactory for many purposes, since each constituent tends to balance the disadvantages of the other. White lead tends to become chalky when exposed to light and weather, while zinc oxide remains hard. Zinc oxide, on the other hand, tends to become brittle, to crack and peel, while white lead forms a tougher coating.

Zinc oxide is made by heating the metal in air or by treating its ores in a similar manner.

341. Lithophone. — This new pigment, which is also known under various other trade names, such as oleum white, Beckton white, ponolith, etc., is made by mixing solutions of zinc sulphate and barium sulphide:

$$\underset{\text{zinc sulphate}}{ZnSO_4} + \underset{\text{barium sulphide}}{BaS} \longrightarrow \underset{\text{barium sulphate}}{BaSO_4} + \underset{\text{zinc sulphide}}{ZnS}$$

Both of the products are insoluble in water. If the mixture of precipitates is heated to dull redness and plunged into cold water, then ground, a pigment is obtained that is brilliantly white, fine in texture, and of good covering power. It has the disadvantage, however, of discoloring when exposed to strong sunlight.

342. Inert Pigments. — These are used as diluents or extenders, and are, in a sense, adulterants, since they diminish the covering power of the paint and the ease of its application. Many of them, however, give increased durability, and they are much used in ready-mixed paints. Both the government and large corporations allow the use of extenders in considerable amounts. In view of this fact, we can scarcely consider their use an adulteration in the making of ready-mixed paints.

The compounds most frequently used as diluents or fillers are: silica in various forms, China clay, barium sulphate (barytes), calcium carbonate in the form of whiting or very finely ground marble, and hydrated calcium sulphate (gypsum). Each of these has its especial advantage of cheapness or other merit. Silica produces a surface that wears well and can be readily repainted. It is claimed that barium sulphate and gypsum especially increase the wearing qualities. The Pennsylvania Railroad has allowed as much as 70% of gypsum in its car paint.

COLORED PIGMENTS

343. The Nature of Colored Pigments. — The body of a paint is usually a white pigment which serves as a paint base and does the greater part of the covering. But if color is desired, some substance of high coloring power is added. This substance should possess, like the white pigment, the fundamental characteristics of permanency, insolubility, opaqueness, and covering power. Colored pigments are usually metallic oxides, sulphides, or other insoluble salts. Occasionally pigments are metallic derivatives of organic dyes; these are termed *lakes*. As a rule, lakes are not very permanent, but several important red lakes have come into use.

344. Red Pigments. — Various forms of ferric oxide, Fe_2O_3, mixed with different proportions of silica or calcium sulphate, give the important reds known as *Venetian* and *Indian* reds (Fig. 99, Frontispiece). These shades resemble the color of red bricks, which have the same coloring matter. *Vermilion* is a sulphide of mercury; it is still used in artist's colors, but is being displaced in house paints by a lake known as para-nitranaline red which is fairly permanent. Red lead, Pb_3O_4, mixed directly with linseed oil without the use of a white pigment, has been until recently the standard paint for the protection of iron work. It acts in an unusual way with linseed oil, acquiring a permanent "set" somewhat as plaster of Paris does with water. Specially prepared red lead is used as a substitute for vermilion. *Carmine* is a red lake derived from cochineal.

345. Blue Pigments. — The most important blue pigment is *ultramarine.* Originally the name was applied to the ground mineral lapis lazuli; it was so expensive that it could be used only in decorative work. In 1828 the substance was artificially made by fusing together aluminum silicate, sodium carbonate, sodium sulphate, sulphur, and charcoal. It is of interest to know that it was probably the first coloring matter produced synthetically. It is one of the most satisfactory of all pigments, and is wonderfully permanent when used under the proper conditions. *Cobalt blue* gives a very fine shade of color. It was originally produced as a combination of cobalt phosphate and aluminum hydroxide, but it is now a special variety of ultramarine. *Prussian blue* has extraordinary coloring powers. It is produced by obtaining a precipitate from the action of ferrous sulphate with potassium ferrocyanide; this precipitate has a bluish white color, but when this is treated with oxidizing agents, the deep blue pigment is obtained. It can also be made directly by the addition of potassium ferrocyanide to a ferric chloride solution, but this is not cheap enough to be used as a commercial method. The permanency of Prussian blue is much disputed. When the precipitate is thoroughly washed to free it from adhering salts, it is said to be highly permanent.

346. Yellow Pigments. — Lead chromate, known as *chrome yellow*, is an intensely yellow pigment that can be obtained in several different shades from bright lemon to deep orange. It is made by the addition of potassium bichromate solution to lead nitrate:

$$\underset{\substack{\text{lead}\\ \text{nitrate}}}{2\,Pb(NO_3)_2} + \underset{\substack{\text{potassium}\\ \text{bichromate}}}{K_2Cr_2O_7} + \underset{\text{water}}{H_2O} \longrightarrow$$

$$\underset{\substack{\text{lead}\\ \text{chromate}}}{2\,PbCrO_4} + \underset{\substack{\text{potassium}\\ \text{nitrate}}}{2\,KNO_3} + \underset{\substack{\text{nitric}\\ \text{acid}}}{2\,HNO_3}$$

The varying shades are produced by adding different acids or alkalies to the solution. Chrome yellows are very permanent. *Yellow ocher* is a beautiful pigment that is obtained from a natural mineral containing hydrated ferric oxide and clay. On being heated, this mineral turns to a red orange color known as *burnt sienna.* *Cadmium yellows* are somewhat like chrome yellow, but richer and more permanent. Their use, on account of their high cost, is almost entirely restricted to artist's colors. They are various forms of cadmium sulphide, CdS. *Litharge*, lead oxide, PbO, is of a dull ocher color. It is made by heating lead in air at a low temperature.

Red, blue, and yellow are fundamental as pigments, since all other colors can, theoretically at least, be obtained from them.

347. Green Pigments. — Greens are usually mixed from blue and yellow pigments, such as ultramarine or Prussian blue and chrome yellows. *Paris green*, used extensively as an insect exterminator, is not much used in paint because it is highly poisonous, and fades rapidly. It is aceto-arsenite of copper. *Oxide of chromium*, emeraude green, gives a beautiful shade that is of the highest order of permanency. Its use is very limited because of its high cost.

VEHICLES

348. Linseed Oil. — The great bulk of all painting is accomplished with the aid of linseed oil. This is extracted by pressing the thoroughly ground seed of the flax plant.

If heat is used a larger yield of oil is obtained, but it is much darker in color. The seed yields from 25 % to 32 % of oil. Like the oil obtained from many other seeds, it possesses the property of absorbing oxygen from the air, up to as much as 18 % of its weight, and forming a gum-like substance. When spread as a thin layer on a surface, the oxidation of the oil produces a tough, impervious membrane. Linseed oil, therefore, makes an excellent holder for a pigment. The oil is sold either *raw* or *boiled*. The so-called boiling is really a heating of the oil with certain salts of lead or manganese. By this treatment the tendency of the oil to acquire oxygen is increased and it "dries" more rapidly.

349. Other Vehicle Oils. — *Fish oil* is obtained from menhaden fish, and dries as does linseed oil by absorption of oxygen. When thickened with litharge, it gives a paint that will stand high temperatures. On this account it is used in painting smokestacks.

Chinese wood oil, another drying oil, makes a paint that will last well in a damp atmosphere. It is much used in making enamel paints. It is also now widely used in the preparation of special paints. *Poppy oil* is an expensive, very white oil that is used in mixing artist's colors.

350. Water Paints dry by evaporation. The pigment is held in place by some sort of cementing substance such as glue or casein in alkaline solution. Casein paints may be used for outside work with a fair degree of permanency. *Whitewash* is slaked lime mixed with water; when the mixture is spread on a surface, the lime absorbs carbon dioxide from the air and forms calcium carbonate. This makes a very cheap paint which does well for inside work, but will last only a short time when exposed to weather.

Tempera Painting is sometimes employed in wall decoration. In this process the pigment is mixed with fresh plaster as it is applied. Some of the world's most famous paintings, for example, those in the Sistine Chapel in Rome, were executed in this medium.

READY-MIXED PAINT

351. Holding Pigments in Suspension. — When mixed with linseed oil only, white lead does not form a permanent emulsion. The pigment settles to the bottom of the container, and forms a hard layer if allowed to remain long without stirring. On this account, "ready-mixed paints" were unknown until a few years ago, and paint for each job was mixed fresh by the painter.

It was finally discovered that a water solution of sodium silicate (water glass) would form a permanent emulsion with white lead and linseed oil, and mixed paints based on this principle were put on the market. This paint, however, was not of lasting quality. Later many other "emulsifiers" were found, but with the increasing adoption of zinc oxide and inert extenders, it has been found that a limited per cent of water serves admirably the purpose of holding the solid matter in suspension.

352. Composition of Mixed Paints. — The various paints that are on the market vary widely in composition, and there is, perhaps, no article that has been so much subject to adulteration and fraudulent labeling. This undesirable condition exists because the public is very ignorant of what constitutes a good paint, and because it takes time for a defective paint to reveal itself. The necessity of careful analysis, of weather tests where the paint is exposed under known conditions, and of truthful labeling is just being realized. Associations of paint manufacturers have united to conduct investigations, and some of the states have passed laws regulating the sale of paints and have established stations for testing purposes.

A good mixed paint may contain a considerable quantity of inert filler, such as silica or powdered marble. As a base, it should have a mixture of white lead and zinc oxide, or one of the lead-zinc pigments, or perhaps lithophone for certain uses. As a vehicle, it should have linseed oil; for special paints it may have fish oil or Chinese wood oil. To hold the solids in suspension, not more than 2% of water may be allowed. Some of the patent emulsifiers do not harm the paint; those which are solutions of rubber are considered allowable; others that are essentially good oil varnishes may even improve the quality. Those that are water solutions of alkaline salts, or those that contain cheap varnishes made from rosin and lime are harmful. Good mixed paint should not contain benzine or other mineral oil.

353. Enamel Paints and Floor Paints. — In these paints certain similar special characteristics are required. They should dry rapidly and should give a surface that is both tough and hard, and they should be able to withstand water. Lithophone is said to make an ideal pigment, and Chinese wood oil a good vehicle. Good resin-oil varnish is added to insure rapid drying and a tough surface. A considerable quantity of inert filler is also frequently used.

354. Stains. — The purpose of a stain is primarily to color a surface, and hence covering power is not desired. Consequently, little or no white pigment is used, and the color is sometimes furnished by a dye instead of a pigment. A small quantity of starch or silica is sometimes used to give a slight body to the stain. *Water stains* and some of the newer stains that are made with benzine, wood alcohol, or acetone are merely dyes, and do not in any sense form a protective coating. *Oil stains* use turpentine and linseed oil, and are used where a "mat" or soft finish is desired. *Varnish stains* dry very quickly and give a polished, shiny surface. As the name implies, the vehicle is mainly varnish.

355. Japan and Driers. — Raw linseed oil absorbs oxygen from the air very slowly, and a paint made with its aid, if allowed to harden naturally, would gather a large amount of dirt and dust. To hasten the process *driers* are added to the oil. Japan driers are made by fusing resins with metallic bases and diluting the product with benzine or turpentine or a mixture of both. Oil driers are made by heating linseed oil with lead or manganese compounds until a thick product is obtained, and diluting the product with benzine or turpentine.

Driers are good examples of catalytic agents. A small amount of drier will hasten the hardening of a very large amount of oil; from $\frac{1}{2}$ to 1 % of the weight of the oil is usually sufficient.

VARNISHES

356. Quality in Varnishes. — A varnish is a finishing or protective coat that is transparent and reveals the grain of the wood. As with mixed paints, there is a great variation in the quality of varnishes as found on the market. A good varnish should stand water, and should not "dust" when scratched. The water test is very easily made by allowing a wet sponge to stand on the surface over night. If the quality is good, either no spot at all, or one that disappears very quickly, will form where the water touched the varnish. The "dusting" is tested by pushing the point of a knife across the surface. A poor varnish will break into a powder which will fly from the point, while a good article will yield a fine ribbon as the knife point plows into the surface.

357. Classification of Varnishes. — Varnishes may be grouped into three classes. *Spirit varnishes* are made by dissolving gums or resins in volatile solvents such as wood, or grain alcohol. These dry by simple evaporation of the solvent, and the gum is left unchanged except that it has been spread out in a thin film. To this class belong the varnishes known as shellac, mastic, sandarac, and dammar. *Turpentine varnishes* are made by dissolving gums in hot turpentine. As these dry, the oil becomes resinous, and the resulting film is tougher, as a rule, than that obtained from spirit varnishes. The most important are the *oil varnishes*, made by dissolving a melted gum in hot linseed oil. These afford very tough, water-resisting films. The gums used are copal, anime, dammar, and amber.

358. Adulteration in Varnishes. — Ordinary rosin is obtained in large quantities in the making of turpentine from coniferous trees. It is largely used as an adulterant of expensive gums used in varnish making, and also as the foundation of a very inferior varnish much used on cheap furniture. The rosin is fused with quicklime and the product used as a gum. It gives a brilliant, but very brittle, varnish.

SUMMARY

Paints are mixtures of *pigments* and *vehicles*.

A Good White Pigment must have high covering power, must mix well with the vehicle, forming a combination that will spread well with the brush, and must resist the action of weather and light. Important white pigments are: *white lead, zinc oxide, sublimed white lead* (a mixture of lead sulphate and zinc), and *lithophone.*

Extenders or Inert Pigments are much used to improve the wearing qualities of paint, although they diminish the covering power and the ease of its application. Important diluents of this sort are: finely ground barium sulphate, marble, chalk, silica, and China clay.

Colored Pigments should have permanency and high coloring power. They are frequently oxides or sulphides of metals. Among important pigments are the ochres and siennas, derived from natural minerals containing ferric oxide and clay, red lead, litharge, vermilion, various lakes, ultramarine blue, cobalt blue, Prussian blue, chrome yellows (lead chromates), cadmium sulphide, oxide of chromium.

Linseed Oil is the most important vehicle. It hardens by absorption of oxygen. Boiled linseed oil is oil that has been heated with lead or manganese compounds; it "dries" more rapidly than the raw oil. *Fish oil, Chinese wood oil*, and *poppy oil* also harden by absorption of oxygen.

Water with glue, casein, or linseed oil soap serves as a vehicle in so-called *water paints.*

In **Ready-mixed Paints** the principal difficulty to overcome is the tendency of pigments to settle as the can of paint stands. To counteract this, an emulsifier is used. Two per cent of water will answer the purpose, and other devices are used.

Stains differ from paints in having very slight covering power.

Japan and other Driers are compounds formed by heating linseed oil with lead or manganese compounds. They act catalytically to hasten the absorption of oxygen by the paint.

Varnishes differ from paint in having a transparent gum instead of pigment to give body to the protecting coating.

Good varnishes do not turn white in contact with water, and on drying leave a tough rather than a brittle coating. *Spirit* *varnishes* dry by evaporation of the volatile solvent in which the gum is dissolved. *Turpentine* and *oil varnishes* dry by absorption of oxygen, and are best for most purposes. Oil varnishes are made by dissolving melted gums, such as copal and dammar, in hot linseed oil.

The Chief Adulteration of Varnishes is in the use of ordinary rosin in place of better gums. It makes a brittle varnish that readily turns white with water.

EXERCISES

1. Why is white lead such a good paint base?

2. How is white lead made? How is zinc oxide made?

3. What is lithophone? How is it made? What is sublimed white lead?

4. Would ground marble, or silica, alone make a good paint base? Why? What advantages has it as a filler?

5. What is the composition of white lead? Which constituent gives the desirable characteristic of making it mix well with linseed oil?

6. What disadvantage is there in the use of zinc oxide as a paint base?

7. Lead sulphide is a black substance. Why do artists in making mural decorations for cities where much coal is burned prefer zinc oxide or a mixture of zinc oxide and lead sulphate as their paint base?

8. Name five very permanent colored pigments.

9. Why is a considerable amount of white pigment used in all paints?

10. Which is more important in a colored pigment, covering power or tinctorial power?

11. Why are dyes not used more frequently to furnish the coloring matter of paints?

12. In making paints why is it important to have pigments ground extremely fine?

13. What is meant by the term "drying oil"? Name four drying oils. Does oil paint lose or gain in weight in drying? Why? Water paint?

14. Why is linseed oil so commonly used as a paint vehicle? How is it made? What is the difference between raw and boiled oil?

15. What particular advantage has fish oil? Chinese wood oil?

16. Of what advantage is it to the consumer to be able to buy ready-mixed paint?

17. What was the chief difficulty to be overcome in making ready-mixed paint?

18. What qualities would be given to a paint by the addition of varnish? For what purposes would such a paint be desirable?

19. What are the tests for a good varnish?

CHAPTER XXXII

DISTILLATION OF PETROLEUM, WOOD, AND COAL

359. Crude Petroleum. — Petroleum is an oily liquid found in the earth. It varies in color from light yellow to black and ranges from a thin to a very thick, sticky liquid. The most commonly accepted theory of its origin is that it was formed by the decomposition of animal or vegetable matter or both. This country is the largest oil producer. Among its well-known oil fields are those of Oklahoma, California, Illinois, Texas, and Pennsylvania with states adjoining it. The largest foreign fields are those of Russia, Galicia, Rumania, and the East Indies.

FIG. 100.—SPOUTING OIL WELL.

Petroleum occurs in oil-bearing sandstones and conglomerates, called "oil sands." It is obtained by drilling wells through the overlying strata, sometimes to a depth of 3000 feet. The rock at the bottom of the well is often shattered by the explosion of several gallons of nitroglycerin; this is called "shooting the well." Only a small portion of the petroleum is now refined in the oil fields, the greater part being transported and refined at the seaboard. In one pipeline in this country, oil is pumped from Oklahoma to the Atlantic coast, a distance of 1600 miles.

REFINING OF PETROLEUM

360. Object. — As petroleum is a complex mixture of the paraffin hydrocarbons having different boiling points, the refining process is chiefly one of fractional distillation. After the distillation follows the removal of impurities that would interfere with the use of the oils. The fractional distillation is conducted according to the nature of the oil and according to the nature of the products desired.

361. Crude Oil Stills. — The crude oil is heated in stills, which are steel boilers, set in brickwork, each with a capacity of 1000 to 1200 barrels. The stills, which are often arranged in pairs, are heated by furnaces extending the entire length of one side of each still. The fuel is either oil, coke, or coal, depending upon the relative cheapness at the refinery. A series of condensers provide for the condensation of vapors according to their boiling points. An arrangement of pipes is used to run the fractional distillates into tanks in accordance with their specific gravities. Coke is left as a residue in the still, and has to be removed before another charge of oil is run in.

A good idea of the refining process may be obtained from the diagram (Fig. 101). A mixture of vapors passes out from the top of the still through a large iron pipe to the bottom of the condenser *B*. The lower half of this is a brick tower filled with cobblestones resting on a grating. Above the cobblestones are more than 50 vertical pipes held in place by a perforated iron plate at the top of the tower. Condenser *C* is similar in construction to condenser *B*. The bottom discharge pipe from *B* is a long coil. The bottom discharge pipe from *C* and the pipe coming out from the top of *C* are each connected with a large coil of pipe in the tank *D*, through which water circulates. Each of these condensing coils delivers a stream of oil to the "running house," where the "still-man" watches the streams of oil and from time to time takes their specific gravity. Movable boxes, with a pipe connection beneath, seen at *E*, permit him to direct the stream from any one of the spouts into the tank which temporarily stores the oil of a specific gravity between certain limits.

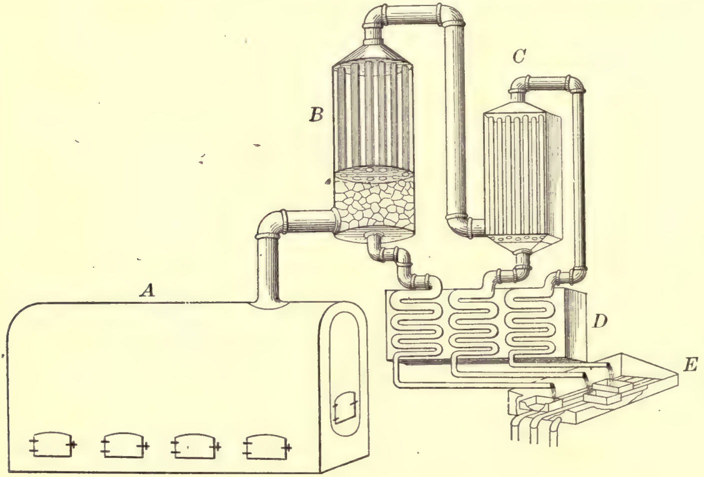


FIG. 101. — FRACTIONAL DISTILLATION OF CRUDE PETROLEUM.

In describing the distillates, it is convenient to use the term *heavy*, meaning oils of high boiling points, which are easily condensed. *Light* means oils of low boiling points. In the early part of the distillation the heavy oils are condensed in the cobblestone part of the tower and run back to the stills through a small pipe. Vapors that pass through the cylindrical tower, but which are too heavy to rise through the rectangular tower, flow out at the bottom of the tower through a cooling coil in the tank and are conducted to the running house. This stream is known as the *intermediate* or *gas oil.* When the intermediate distillate shows a specific gravity of 0.85 in the running house, the run-back to the still is closed. The distillate from the bottom of the cobblestone tower then runs down through a coil in the tank and is known as the *paraffin oil distillate.* The light vapors, which pass through both towers, pass downward from the top of tower *C* through a pipe to a cooling coil, which discharges in the running house. This stream, which is termed crude naphtha, contains *gasoline*, *benzine*, and *kerosene*, the light oils. Thus at this stage of the process the three streams in the running house are the paraffin oil distillate, the intermediate oil, and the crude naphtha or light oil.

362. Steam Stills. — The intermediate oil and the light oil are again fractionally distilled in steam stills and the distillates separated according to their specific gravities. The oil to be distilled is pumped from the running house to another cylindrical still heated by either live or exhaust steam. A continuous stream of oil flows into the steam still at the bottom, and a continuous stream of vaporized oil passes out at the top. Fractional distillates of a similar range of specific gravities are sometimes combined and again steam-stilled. The object of these repeated distillations is to get definite grades of oil of certain specific qualities.

Thus the crude naphtha, which is the *light oil distillate* having specific gravity of 0.73 or less, yields a number of fractions. The more important of these in the order of the increasing specific gravity, are petroleum ether, naphtha, and benzine. All these are trade names given to mixtures of varying composition. In some cases the trade name may cover several grades, each of which is sold according to a definite specific gravity and an approximate boiling point. Thus there are several benzines and several naphthas on the market.

From the distillates with a specific gravity above 0.73, but below 0.83, coming from either the crude oil still or the steam still, there are obtained the burning oils or kerosenes. These oils are distilled to a definite specific gravity and *fire test*, the temperature at which the oil gives off enough vapor to maintain a continuous flame if ignited. Thus the best grade of kerosene sold in this country, *water white*, has a fire test of 150° F. (65.5° C.). Common refined oil, known as *export oil*, has a fire test of 110° F. (43.3° C.). The burning oil distillates which do not have a good color are run into the gas oil distillate, which is used for carbureting water gas (§ 371).

363. Removal of Impurities. — All the burning oils when they come from the still contain impurities which interfere with their burning qualities. These foreign substances are removed in the *agitators*. The oil is first treated with concentrated sulphuric acid, then washed with water. It is next treated with sodium hydroxide or carbonate to neutralize the acid, and again washed with water. During each of these operations, the mixture is stirred violently by a powerful air blast. The oil is finally treated with fuller's earth to clarify or brighten it. From the agitators the oil is run into settling tanks, in order to remove the water and the fuller's earth, and then goes to the storage tanks.

Canadian petroleums and some of those from the Middle West contain sulphur compounds, which give an offensive odor in burning. As these compounds are not removed by the usual processes of refining, special means have been devised for their elimination, viz., distillation in the presence of copper oxide. By this distillation, carbon disulphide, methyl sulphide, and other sulphur compounds are removed.

364. Paraffin Oil Distillate.—This is subjected to redistillation, and other processes are also employed, such as chilling and squeezing in filter presses to separate waxes, sweating with steam, and treatment with sulphuric acid. A wide range of products is obtained—lubricating oils of low or medium viscosity, heavy lubricating oils, vaseline or petrolatum, soft waxes, and hard waxes, such as the refined paraffin of commerce.

Coke is the residue left in the crude oil still and has to be cleaned out with sharp-pointed shovels. This coke is used in making the carbons for arc lamps, but owing to the oversupply for that purpose much of it is used as a fuel to heat the crude oil stills.

365. Gasoline. — When the supply of gasoline was plentiful enough to meet the demand, it contained the hydrocarbons found in refined naphtha, benzine, and ligroin. As stated in § 361, the vapors of the heavy oils are condensed in the early part of the distillation and run back into the still. There they strike the boiling oil which is raised to a higher temperature and are converted into hydrocarbons of a lower molecular weight and boiling point. This process is called *cracking* and results not only in the formation of lower hydrocarbons of the paraffin series, but ethylene hydrocarbons as well.

The hope of meeting the ever increasing demand for gasoline seems to depend upon processes of converting the heavier oil distillates into the lighter oils. Several such processes are in the last stages of experimental development, with very favorable outlook. Until these hopes are realized, users of gasoline will have to be content with a poor quality, as some of the oils of higher boiling points have to be mixed with the true gasoline fractions to supply the commercial demand for the liquid.

366. Destructive Distillation. — The distillation of petroleum which has just been described is essentially the same as the distillation of a mixture of water and alcohol described in Chapter XVI. In this way a partial separation of the liquids is accomplished, for the first portion of the distillate contains a larger percentage of the liquid having the lower boiling point. When solids, such as wood and coal, are heated out of contact with the air, not only are the liquids present distilled off as such, but, as the temperature increases, some of these liquids and some of the solid compounds present are cracked (§ 365). As a result, vapors of substances that were not present in the original material pass off and are condensed. The process of breaking up a complex substance into a number of simpler substances by heating out of contact with air and condensing the resulting vapors, is called *destructive distillation.*

367. Destructive Distillation of Wood. — The destructive distillation of wood was first carried on simply to obtain charcoal. Wood was piled loosely and the whole pile covered with turf. The wood was set on fire and a portion of it allowed to burn in a limited supply of air entering through air holes in the turf. The heat of the burning wood was enough to drive off the volatile matter from the remainder of the wood. The volatile products were allowed to escape. To-day we realize that these volatile products are more valuable than the charcoal.

Until wood became too valuable, it was used in making illuminating gas.

In a modern plant, the destructive distillation of wood is carried on in retorts or in rectangular ovens. The charge varies from one half a cord to five cords of wood, in the form of cord wood or billets or chips. The charcoal remains in the oven or retorts, while the volatile products pass into a vertical, tubular condenser kept cool by water circulating in an outer shell. The materials recovered consist of *gases*, which are used as fuels; a water solution, known as *pyroligneous acid;* and *tarry substances.*

The condenser liquor from the distillation is usually in three layers: an upper layer of tarry oils, an intermediate layer of pyroligneous acid, and a lower layer of tar. The pyroligneous acid contains acetic acid, wood alcohol, acetone, and certain other compounds.

The pyroligneous acid is usually distilled; the volatile wood alcohol passes off first and is later purified. The acetic acid follows. The latter is called distilled "wood vinegar." It is neutralized with lime forming *gray acetate of lime*, or with sodium carbonate. Acetic acid is obtained from calcium acetate or from sodium acetate by distilling an excess of either of these salts with concentrated hydrochloric acid. The distillate is redistilled over calcium acetate to remove any hydrochloric acid that came over with the acetate acid. Glacial acetic acid is made by distilling pure anhydrous sodium acetate with concentrated sulphuric acid.

Acetone, $CH_3 . CO . CH_3$, distills over with the wood alcohol and is separated from it with difficulty. Commercially acetone is made by the dry distillation of the gray acetate of lime.

In the distillation of *hard wood*, charcoal, alcohol, and acetates are the main products.

Resinous woods yield tar, turpentine, and charcoal. The distillation of wood has become a very important and highly specialized industry.

368. Destructive Distillation of Coal. — The manufacture of illuminating gas from coal is a process of destructive distillation. The bituminous coal used contains from 30 % to 40 % of volatile matter and is heated in iron retorts. The heat must be sufficient to carbonize the coal and be maintained long enough to complete the decomposition and the distillation.

The first step in the carbonization begins at 400° C. and is probably a fusion, as the temperature remains constant for some time. As the heat increases, the carbon compounds produced in the first stage split into simpler compounds. Some of these, striking the very hot sides of the retort, undergo further reactions resulting in the formation of complex compounds. The temperature and time taken for the distillation determine in great measure the relative amounts of the various gaseous products. It has been found desirable to have the pressure in the retorts approximate that of the outside air. A pump known as the *exhauster* brings this about.

In a modern gas plant, ingenious mechanical devices are used for charging, opening, and emptying these retorts (§ 370, Fig. 102). The quality of the coke obtained depends upon the time and temperature of the destructive distillation. A low temperature and a short time give a soft porous coke containing 12 % of volatile matter. As the temperature increases and the time lengthens, a harder, denser coke of a metallic appearance, suitable for foundry purposes, is obtained.

The products that pass out of the retorts are illuminating gas with various gaseous impurities, an ammoniacal liquid, and coal tar vapor or fog. The non-condensible gaseous impurities are chiefly ammonia, NH_3, cyanogen, C_2N_2, hydrogen sulphide, H_2S, and carbon dioxide, CO_2. The coal tar contains a number of organic (carbon) compounds. The valuable by-products of the process, then, are coke, ammonia, and coal tar products. It has been estimated that a ton of gas coal of average quality yields about two thirds of a ton of coke, 13 gallons of tar, 20 pounds of ammonium sulphate (from the neutralization of the ammonia water), and 12,000 cubic feet of gas. The coal tar is collected from the various gas plants and a number of valuable carbon compounds are extracted from it in an establishment devoted to that purpose. Among these compounds may be mentioned naphtha, benzene, toluene, heavy oils, carbolic acid and its derivatives, and naphthalene, familiar in its crude form as moth balls.

In a gas plant, there are three main steps in the separation of the products leaving the retorts, the removal of the coal tar, the removal of the ammonia, and the purification of the illuminating gas from gaseous impurities. The action in each part of the apparatus is briefly stated in the following section.

369. Steps in the Manufacture of Illuminating Gas. —

Retorts. A carbonization of soft coal, leaving coke in retort; gases and tarry smoke pass to hydraulic main.

Hydraulic main. Part of tar condensed and deposited; some ammonia dissolved.

Primary condenser. Gas and tarry vapor cooled; some tar deposited.

Tar extractor. Tar is removed.

Exhauster. Proper pressure maintained in retorts; gas forced through train of scrubbers and purifiers.

Naphthalene scrubber. Naphthalene absorbed by some heavy tar oil.

Cyanogen scrubber. Cyanogen absorbed by alkaline solution of ferrous sulphate.

Secondary condenser. Gases cooled so that the remaining ammonia may be absorbed by water in the ammonia washer.

Ammonia washer. Remaining ammonia absorbed.

Purifiers. Hydrogen sulphide absorbed by ferric oxide. (Sometimes additional purifier for removal of organic sulphur compounds.)

Holder. Gas ready for distribution.

370. Continuous Process.—In Fig. 102 is shown a sectional view of a gas retort, in which the process goes on without interruption for removing coke from the retorts and inserting a fresh charge of coal. The retorts, a section of one of which is shown, are vertical and increase in diameter from top to bottom. The coal is admitted through the coal gate at intervals from the storage bin on the top floor to the charging hopper immediately below. From this hopper it falls continuously into the retort below, as needed. This retort is heated by the combustion of producer gas from the gas producer on the furnace floor. The hot gases from the producer first strike the retorts near the top and then are forced to pass around and downward between the retorts, as shown by the arrows. After parting with most of their heat, these gases finally escape into the chimney.

The gas coal in the retort begins to distil at the top where the heat first strikes it. As the coal works down in the retort the proportion of coal decreases and that of coke increases, as shown in the illustration. The illuminating gas works its way upward to the pipes marked

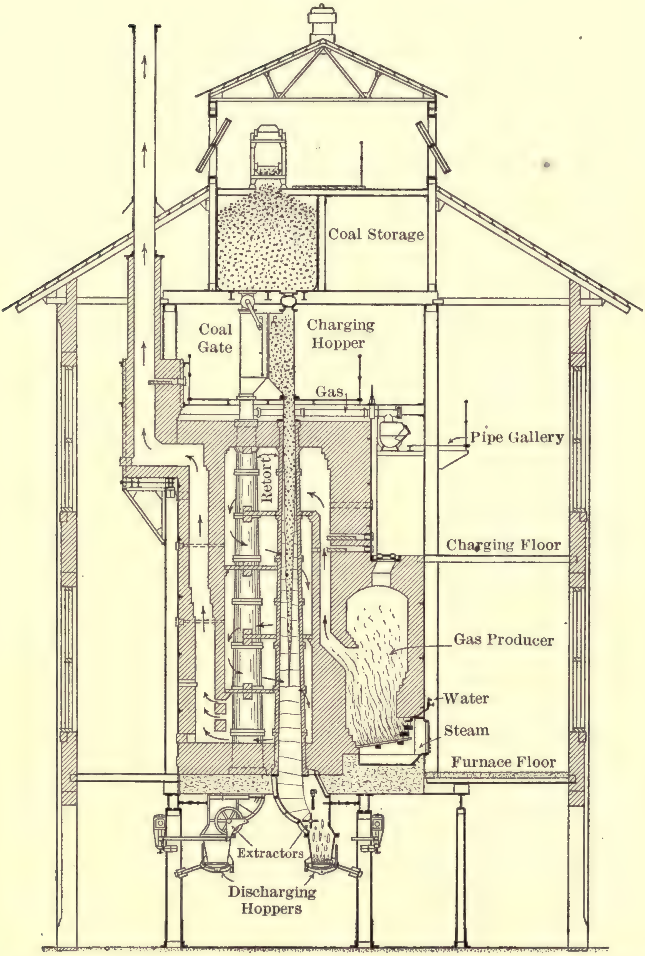

Coal Storage
Coal Gate
Charging Hopper
Gas
Pipe Gallery
Retort
Charging Floor
Gas Producer
Water
Steam
Furnace Floor
Extractors
Discharging Hoppers

FIG. 102. — VERTICAL RETORTS OF THE CONTINUOUS PROCESS FOR MAKING ILLUMINATING GAS.

"Gas" and through them to the hydraulic main on the pipe gallery. It is then purified as outlined in § 369. The compact mass of coke at the bottom is broken up by the extractors shown at the bottom and falls into discharging hoppers, from which it is periodically removed. Vertical retorts operated in this way yield more gas per pound of coal and gas of higher illuminating power than horizontal or inclined retorts, in addition to avoiding the labor and loss of time involved in cleaning and discharging horizontal, intermittently operating retorts.

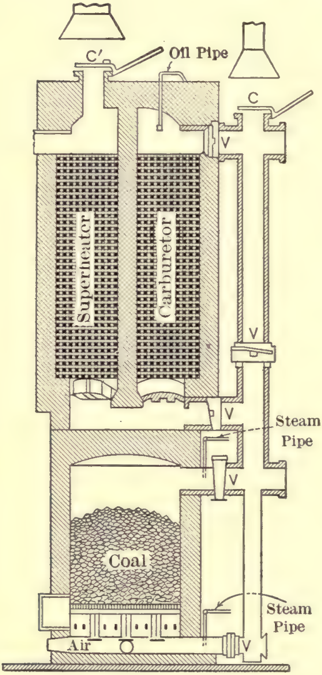


FIG. 103. — WATER GAS GENERATOR.

371. Commercial Manufacture of Water Gas. — The essential steps in the manufacture of water gas for illuminating purposes and for producer gas have been already described in §§ 96, 97. For purposes of comparison with illuminating gas and because the two illuminants are often made in the same plant, a few details of a modern water gas generator are given here. The generator shown in Fig. 103 has the carburetor and superheater placed directly above the fire chamber, and permanently connected with each other by an opening at their lower ends. Valves are located in the connecting gas passages at the points marked *V*. The caps

C and C' are valves opening into stacks leading to the air.

In starting the operation of the generator, a blast of air is blown up through the hard coal or coke from below, the cap valve C and the other valves between it and the fire chamber being open. In this way the coal is soon brought to incandescence. The cap C is then closed and the valve leading into the upper end of the carburetor is opened. This permits the heated gases to pass down through the *carburetor*, which is a chamber filled with a checkerwork of brick, and up through the *superheater*, a similar chamber, then out through C', which is opened for the purpose, into a stack. This is called the "blow" and is continued until the carburetor and superheater have reached the proper working temperature.

The air blast is then shut off and steam is admitted through one of the steam pipes and, at the same time, gas oil is sprayed into the carburetor through the oil pipe. The steam in passing through the incandescent coal reacts with it, with the formation of carbon monoxide and hydrogen.

$$\underset{\text{carbon}}{C} + \underset{\text{steam}}{H_2O} \longrightarrow \underset{\text{carbon monoxide}}{CO} + \underset{\text{hydrogen}}{H_2}$$

This mixture is *enriched*, that is, given added illuminating power, by taking up gases produced by the cracking of oil in the carburetor; the cracking process is continued and the mixture is made uniform by passing through the superheater. The cap valve C' is closed and the enriched gas passes out through the pipe toward the left at the top of the superheater.

The carburetor in a water gas plant is likely to become overheated, as the gas passes directly from the fire chamber into it. By proper manipulation of the valves of the generator shown in the illustration, when the carburetor is sufficiently heated, the gas may be "by-passed," that is, the gas from the fire chamber may be passed below the carburetor directly across to the superheater. The oil gas from the carburetor will be forced into the water gas as the latter passes through the intermediate chamber between carburetor and superheater, and the oil and water gas will be thoroughly incorporated in the superheater. By other arrangements of the valves, the temperature of all parts of the apparatus may be completely controlled.

When the coal becomes cooled below the proper temperature, air is again blown through it and out through *C* and the entire process just described is repeated. The steam is blown up through the coal at the beginning of the "run" and down through it during the latter part.

SUMMARY

Petroleum is an oily liquid found in the earth and is a complex mixture of hydrocarbons.

Refining of Petroleum consists in the fractional distillation of the crude petroleum and the removal of impurities from the fractionated portions. The products include light and solvent oils like petroleum ether, naphtha, benzine, and gasoline ; burning oils like kerosene ; light and heavy lubricating oils ; and waxes of varying hardness.

Destructive Distillation is the breaking up of a complex substance by heating without access of air, into a number of simple substances which are evaporated and then condensed.

Destructive Distillation of Wood yields tar and tarry oils, pyroligneous acid, combustible gas, and a residue of charcoal. From the pyroligneous acid wood alchohol, acetone, and acetic acid are obtained.

Turpentine is one of the products of the destructive distillation of resinous woods or of the pitch obtained from resinous trees.

Destructive Distillation of Soft Coal yields illuminating gas, ammoniacal liquor, coal tar, and a residue of coke. Ammonia is extracted from the ammoniacal liquor and many valuable carbon compounds from the coal tar. Several impurities must be removed from illuminating gas before it is fit for burning.

Water Gas is made by steam passing through incandescent hard coal or soft coke, and is enriched by incorporating oil gases of high illuminating power with it. The process of manufacture is intermittent.

EXERCISES

1. What is petroleum? What are "oil sands"? What is meant by "shooting a well"?

2. What is a crude oil still? How is it heated? What is left in it at the end of a distillation?

3. Show how the construction of the cobblestone tower makes it a more efficient condenser than the rectangular tower.

4. Why do the cobblestone and rectangular towers have discharge pipes at both the top and the bottom?

5. Why is cold water kept circulating in tank *D* (Fig. 101)? Why do not the pipes run straight through?

6. Describe the duties of the "still man" in the running house.

7. Why are some of the condensed vapors from the crude oil allowed to run back to the still?

8. What is accomplished by the steam stills? How do they operate?

9. What are the agitators? In purifying the fractional distillates, what is the use of the sulphuric acid, the sodium carbonate, and the water?

10. Why has the quality of commercial gasoline deteriorated in recent years?

11. What is meant by the "cracking" of oils?

12. What is destructive distillation?

13. What is pyroligneous acid? Charcoal?

14. Why is not acetone obtained directly from the destructive distillation of wood? Trace the commercial process for making acetone indirectly from wood.

15. Why is soft coal used for making illuminating gas?

16. What are the three main steps in separating the products leaving the retorts in a coal gas plant?

17. Name three common coal tar products.

18. Explain the use of the fire chamber, the carburetor, and the superheater in an enriched water gas plant.

19. Write an equation for the preparation of unenriched water gas. What is "enriching" and how is it accomplished?

20. Explain why the enriched water gas plant described is economical in space, and efficient in the control of the temperature of all parts of the apparatus.

21. Why is soft coal not used in a water gas plant?

CHAPTER XXXIII

BLAST LAMPS AND BLOWPIPES

372. Blast Lamps. — One of the most familiar facts regarding combustion is that the greater the draft, the hotter the fire. The blacksmith, having a considerable supply of solid fuel in the forge, increases the rapidity with which the fuel burns, and so raises the temperature, by blowing a blast of air through the incandescent coal by means of his bellows. In the bunsen burner, as has already been shown (§ 105), the air is drawn in through the orifices in the side of the burner tube in a comparatively slow stream. The resulting flame is large in size and of moderately high temperature. Now the amount of heat produced when a cubic foot of gas is burned is the same, whether it burns slowly or rapidly; but the temperature produced is much greater when the gas burns rapidly than when it burns slowly. Therefore if either gas, air, or both are supplied to the burner under pressure, so that they will flow to the flame more rapidly, the combustion will be more rapid and the temperature higher. The flame will also be smaller, and so the heat will be concentrated to a greater extent.

Gas burners to which one or both of the gases taking part in the combustion are supplied under pressure are called *blast lamps* or *blowpipes*. A simple example is found in the laboratory blast lamp (Fig. 104). Gas is brought to the burner through one of the rubber tubes and admitted to the large outer tube of the burner. Air, supplied under pressure from a bellows or an air compressor, is brought through the other rubber tube and admitted to a small tube placed in the center of the large tube. It will be noticed that the arrangement of air and gas in the blast lamp is just the reverse of that in the bunsen burner. The proportion of gas and air supplied to the burner can be regulated by means of the thumb-screws shown at either side of the burner. In operation, the gas is first admitted and lighted, giving a large, sooty, flickering flame. The air is then turned on; the flame becomes much smaller and intensely hot, making a rustling noise as it burns. A properly adjusted blast lamp has a flame with practically no inner cone. The narrowing of the outer tube at the tip causes the gas and air to form a much more intimate mixture than is obtained in the bunsen flame, and so more uniform combustion and a higher temperature result. Blast lamps are used for a great variety of operations in which a temperature higher than that of the bunsen flame is required.

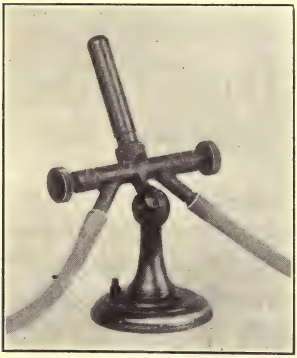


FIG. 104. — LABORATORY BLAST LAMP.

373. The Blow Torch, used by plumbers, painters, and others, is essentially similar to the blast lamp, but uses liquid fuel. The gasoline, or kerosene, is forced up to the needle valve (Fig. 105), by means of air compressed by a pump attached to the torch. The needle valve causes the fuel to flow out in a fine spray, which is easily vaporized. To start the torch, a little fuel is allowed to run out into the heating pan just below the burner, the needle valve is closed and the fuel in the pan is lighted. The flame thus produced heats the metal parts around the needle valve, and when the latter is again opened, the issuing spray is vaporized and so is easily ignited. When the torch is burning, the parts surrounding the needle valve remain hot enough to continue to vaporize the fuel as fast as it is furnished, as in the case of the gasoline stove and gasoline torch (§§ 110 and 115). The air needed for combustion in the torch is drawn in through openings in the sides or bottom of the shield surrounding the needle valve, as in the case of the bunsen burner. In the blow torch it is the fuel vapor which is furnished under pressure.

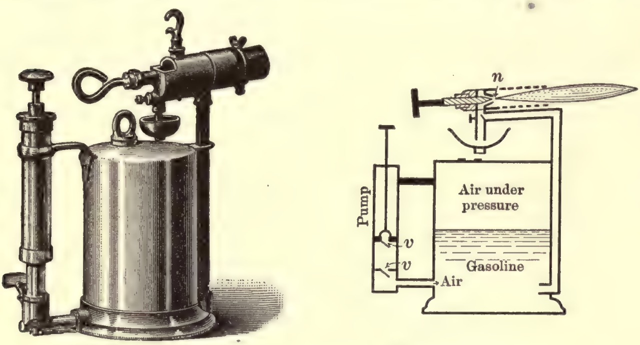


FIG. 105. — BLOW TORCH: *n*, NOZZLE; *v*, VALVE.

374. Oxy-hydrogen Blowpipe. — The intense heat of the hydrogen flame has already been noted (§ 4). The maximum temperature of this flame can be obtained by using a mixture of 2 volumes of hydrogen to 1 of oxygen — the proportion in which the two gases unite to form water. As this mixture of hydrogen and oxygen is highly explosive, special precautions must be taken in burning it. The oxy-hydrogen blowpipe (Fig. 106) is constructed on the same principle as the blast lamp. The hydrogen is lighted first and burns in air, then the oxygen is turned on. Both gases for this blowpipe are always used under pressure. There are three reasons for this. In the first place, the rapidity of burning is increased by compressing the gases and the temperature of the flame correspondingly increased. Secondly, the rapidity with which the gases escape from the burner prevents the flame from traveling back toward the hydrogen supply and causing a disastrous explosion. Thirdly, it is more convenient to store highly compressed gases than gases under lower pressure, which consequently occupy a larger volume.

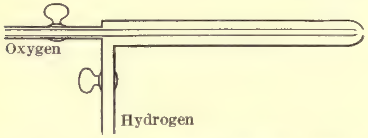


FIG. 106. — OXY-HYDROGEN BLOWPIPE.

By the oxy-hydrogen blowpipe, temperatures of from 2000° to 2500° C. can be reached, the limiting temperature being determined by the temperature at which the water formed in the process begins to dissociate again into hydrogen and oxygen, absorbing heat in so doing. The temperatures obtained are sufficient to melt platinum and silica (§ 474) and the oxy-hydrogen flame is employed for these purposes. Another important use of the oxy-hydrogen flame is in the *calcium* or *lime light*, in which the flame is directed against a stick of lime or calcium oxide (Fig. 4, page 5). The lime is heated to a brilliant white heat, and is used as the source of light for stereopticons and theatrical spot lights. For both of these purposes the calcium light has given place to the electric arc, wherever electric current can be obtained. The oxy-hydrogen flame is also employed in *lead burning*, that is, the joining of sheets or other pieces of lead by melting their edges together.

375. Oxy-acetylene Blowpipe. — The intense heat of the oxy-acetylene flame has been known for a long time. With the improvement in the commercial manufacture of acetylene, the oxy-acetylene blowpipe has been developed until it has become an exceedingly useful tool. By its use, two pieces of metal of almost any kind can be joined completely by fusing them together at the junction, and wrought iron and steel can be cut rapidly and with great convenience.

A complete oxy-acetylene outfit is shown in Fig. 107. At the left is seen the acetylene generator, in the center, the oxygen tank, and in the workman's hand is the blowpipe or "torch" with which the work is done. The acetylene generator has already been described (§ 99). The oxygen is compressed into strong steel tanks. The blowpipe is constructed on the same general principles as

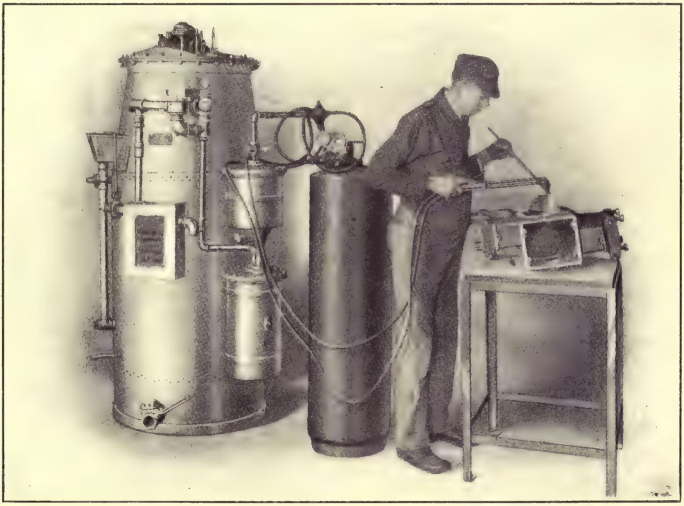


FIG. 107. — OXY-ACETYLENE BLOWPIPE OUTFIT.

the oxy-hydrogen blowpipe, but is somewhat more complicated. It will be remembered that acetylene cannot be safely compressed as a gas to any considerable extent, but that acetone will dissolve several times its own volume of acetylene, which can then be liberated under pressure from the acetone. On these facts depend the construction of two types of blowpipes, the *low-pressure* and the *high-pressure.*

In the low-pressure blowpipe, the oxygen is supplied under a pressure of 15 to 25 pounds per square inch and the acetylene usually at less than 1 pound. The oxygen is carried to the working end of the blowpipe (Fig. 108), through a tube extending through the center of the handle to a fine opening (*a*) at the base of the nozzle. The acetylene, passing through the outer chamber of the handle, enters a space surrounding the oxygen jet. The shape of the passages in the nozzle is such that the oxygen draws the acetylene rapidly into the nozzle and the gases are thoroughly mixed before they reach the tip of the blowpipe, from which they issue at high speed. The pressure of the oxygen can be adjusted by a reducing valve on the oxygen tank, and the amount of each gas is regulated by a separate stopcock. The danger of striking back is averted by the velocity with which the gases issue from the blowpipe, and also by a wire gauze screen (*w*) in

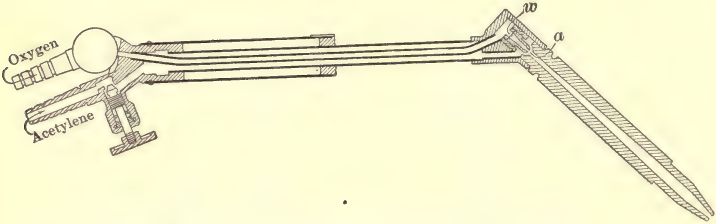


FIG. 108. — OXWELD LOW PRESSURE BLOWPIPE.

the passage at the base of the nozzle, because a flame will not pass through minute holes. The blowpipe just described is used for fusing and welding only. The cutting nozzle will be described later.

For emergency repairs and other cases where it is not convenient to transport the bulky acetylene generator, a cylinder of acetone saturated with 250 times its volume of acetylene under a pressure of 150 pounds per square inch is used. In this case, a different form of nozzle is employed. The low-pressure system, however, is cheaper, and is used if possible.

The complete combustion of acetylene to carbon dioxide and water would require 2.5 volumes of oxygen to 1 of acetylene. But the parts of the oxy-acetylene apparatus are designed so that the acetylene breaks up at the tip of the blowpipe into carbon and hydrogen. Only the carbon burns, while the hydrogen surrounds the flame and acts as a protection against oxidation of the metal. The temperature of the flame is above the temperature at which water dissociates into hydrogen and oxygen, and so the hydrogen does not burn at the jet, but only on the outside of the flame.

376. Autogenous Welding. — When two pieces of metal are joined by running liquid metal of similar character on the surfaces to be united, the process is called autogenous welding. An example is lead burning. The oxy-acetylene blowpipe, producing a temperature of nearly 4000° C., is peculiarly adapted to autogenous welding of even the less fusible metals, like iron and steel. In the case of thin sheets of metal, the edges are brought into perfect contact and then fused together, without the addition of other metal. In most cases, however, a space is left between the pieces and into this space is run fused metal of the same kind, suitable to produce a weld that can be machined. The operator in Fig. 107 is melting the stick of metal which he holds in his left hand for this purpose. This metal used as a "filler" should be rich in the easily oxidizable constituents of the metal to be welded. It is necessary also to use suitable fluxes for the removal of oxides from the molten metal, and to regulate the gases in the blowpipe so that the inner zone of the flame shall be neither oxidizing nor reducing in its action. In welding all but thin metal, the adjacent metal is preheated, so that when the entire piece cools after the addition of the molten metal, it shall be free from strains. Preheating lessens the time of blowpipe heating and so saves gas. Blaugas and oxygen are also used for autogenous welding (Fig. 109) and for cutting.

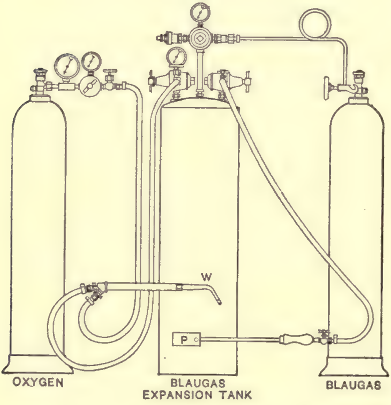


Fig. 109. — Oxy-Blaugas Welding Outfit.

The applications of autogenous welding are very numerous. It is used as a substitute for riveting in the manufacture of steel and iron tanks. The parts of bicycle frames and other articles made of steel tubing, safes, and steel office furniture are welded in this way. It is the means employed in the manufacture of aluminum articles whenever it is necessary to join two parts, as, for instance, welding the spouts into aluminum teakettles. A most important application is in repair work. Here it is used to fill in holes in defective castings, which would otherwise have to be remade, to repair broken machine parts and to build up worn ones, and in the repair of aluminum gear cases and other automobile parts.

377. Cutting. — Another important use of the oxy-acetylene flame, combined with a high-pressure oxygen blast, is in cutting iron, steel, and other metals. The cutting blowpipe has a circle of small oxy-acetylene jets at its point, while in the center is an opening for oxygen at high pressure. The small jets are turned on first, and serve to heat the metal intensely. When the metal has

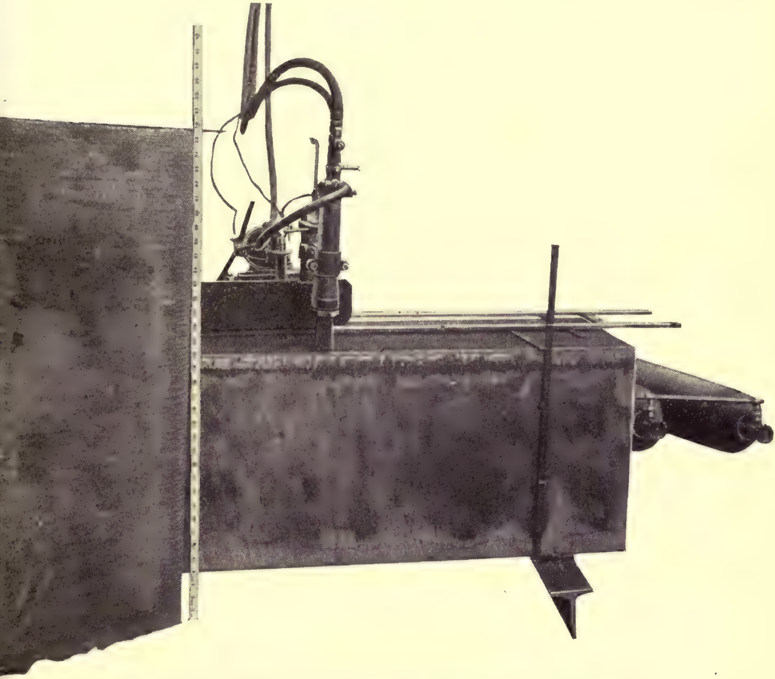


FIG. 110. — STEEL CUT WITH OXY-ACETYLENE FLAME.

been heated to about 1000° C., the jet of oxygen at high pressure is turned on. This oxidizes the metal, and the force of the jet blows out the molten oxide as rapidly as it is formed, thus making a comparatively narrow cut. After the cut is started, the small oxy-acetylene flames aid the process by helping to bring the metal up to its kindling temperature, for the cutting process really consists in burning the iron or steel. Cast iron cannot be cut by this process, but wrought iron, structural steel, armor plate, and many special steels that cannot be cut with tools yield to the combination of intense heat and abundant oxygen. The process is of great service in cutting up scrap iron and steel, in wrecking steel structures, in trimming steel castings, and in trimming away defective parts preparatory to welding. In much of this work, a perfectly even cut is not necessary and the blowpipe is guided by hand. By using proper mechanical means for guiding the torch, very even cuts of any form can be made (Fig. 110).

SUMMARY

Blast Lamps are burners in which an intimate mixture of gas and air issues from the burner with great velocity and burns with a hot, non-luminous flame. They are used in laboratories and wherever a small flame having a high temperature is required.

Blow Torches are blast lamps adapted to the use of liquid fuel.

The Oxy-hydrogen Blowpipe is a burner in which oxygen and hydrogen, both highly compressed, unite and burn with an intensely hot flame. It is used for melting platinum and silica, for the calcium light, and for fusing together the edges of sheets of lead and other metals.

The Oxy-acetylene Blowpipe is similar in construction to the oxy-hydrogen blowpipe. It employs acetylene in place of hydrogen and produces a hotter flame. It is used for the autogenous welding of many metals.

Metals may be cut by burning them with a jet of high pressure oxygen, provided they are heated at the same time with an oxy-acetylene flame.

EXERCISES

1. Compare the blast lamp with the bunsen burner as to (*a*) construction, (*b*) rapidity of combustion, (*c*) temperature produced.

2. Why do blast lamps and blowpipes have an outer and an inner tube?

3. Why is the outer tube narrowed at the end?

4. Give the order of operations in lighting a blast lamp, with the reason for following this order.

5. Why has the flame of the blast lamp very little inner cone?

6. Describe the lighting of a blow torch, stating reasons for each operation.

7. Compare the oxy-hydrogen blowpipe with the blast lamp as to (*a*) construction, (*b*) temperature produced, (*c*) uses.

8. Explain what is meant by autogenous welding, and give examples of its use.

9. What is "preheating," and what is its purpose in autogenous welding?

10. Explain how an oxy-acetylene cutting blowpipe differs from a welding blowpipe.

11. What two purposes does the high-pressure oxygen jet serve in oxy-acetylene cutting?

CHAPTER XXXIV

GAS ENGINES

378. Construction and Operation. — The use of gaseous fuels as sources of light and heat has been followed in recent years by their extensive use for power. The gas engine consists essentially of a cylinder in which a mixture of gas and air burns explosively. The combustion raises the temperature of the gases in the cylinder and so causes them to exert a powerful pressure against a piston. The motion of this piston is transmitted to a crank and flywheel by a connecting rod. The cylinder is provided with valves for admitting gas and air, and for permitting the products of combustion to escape. The mixture of gas and air is ignited at the proper point in the stroke by raising a small portion to its kindling point, usually by an electric spark. The combustion takes place in from $\frac{5}{100}$ to $\frac{28}{100}$ of a second.

Starting with the combustion of the charge, which takes place with the piston ready to begin its forward stroke, the order of events in a "four-cycle" engine is as follows:

(1) the pressure suddenly produced by the burning of the mixture drives the piston forward to the end of its stroke (power stroke);

(2) the energy stored in the flywheel forces the piston back and the burned gases are expelled through an exhaust valve (exhaust stroke);

(3) the piston is again drawn forward by the flywheel and fresh supplies of air and gas are drawn in through

valves which open at the beginning of the stroke (admission stroke);

(4) the flywheel again forces the piston back to the starting position and compresses the new mixture before it is ignited (compression stroke).

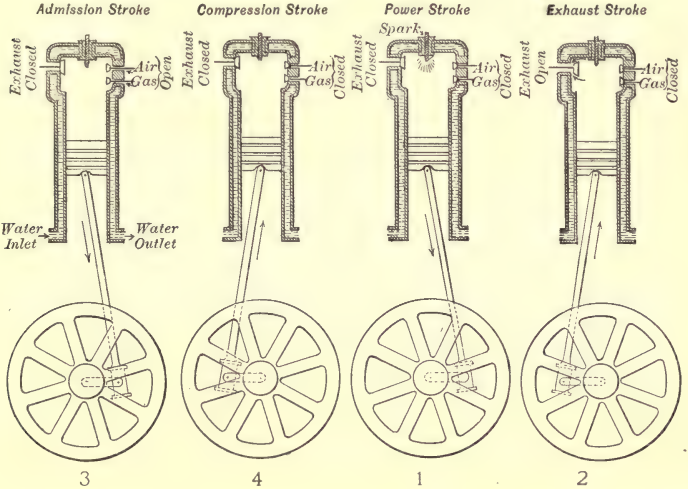

Admission Stroke
Compression Stroke
Power Stroke
Exhaust Stroke
Spark
Exhaust Closed
Air
Gas
Open
Exhaust Closed
Air
Gas
Closed
Exhaust Closed
Air
Gas
Closed
Exhaust Open
Air
Gas
Closed
Water Inlet
Water Outlet
3
4
1
2

FIG. 111. — GAS ENGINE CYCLE.

In this type of engine there is only one power stroke in two revolutions, but the pressure developed is so high that the heavy flywheel easily carries the engine through the other three strokes. The cylinder walls are made hollow, so water can be kept circulating between to prevent overheating.

379. Use of Gas Engines. — Gas engines found their first extensive commercial use in the oil fields, where natural gas, associated with petroleum in origin, frequently flows from the ground in large quantities. This gas has high heating power and consists chiefly of marsh gas, together with some hydrogen and other combustible gases. Thus the oil producer is often enabled to pump his wells without paying any fuel bills. The fact that in internal-combustion engines like the gas engine, the heat is used directly at the point where it is produced, led the oil producer to use a gas engine instead of burning the gas under the boiler of a steam engine. This greater efficiency of the gas engine, and its greater convenience of operation as compared to the steam engine, soon led to the adoption of the gas engine for use with illuminating gas for small power plants, although the usual price of gas was too high to permit its economical use for large plants. The question of expense is now met by individual gas plants for each power plant, because about twice as much power can be produced from a ton of coal by means of a gas producer and a gas engine as by a steam boiler and steam engine.

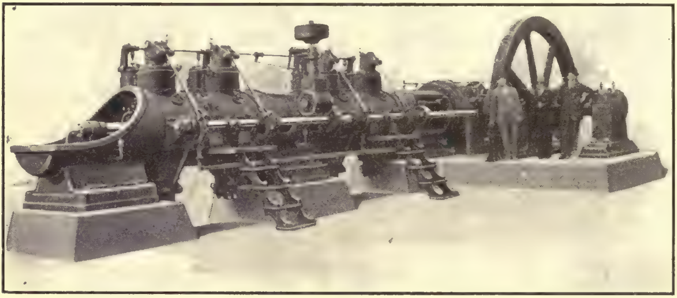


FIG. 112. — LARGE GAS ENGINE FOR POWER PLANT.

380. Gas Producers. — The gas producer (Fig. 113) is not unlike an ordinary coal stove in its construction and action. It is a vertical closed cylinder containing a deep bed of coal, resting on a bed of ash. The coal is lighted at the bottom and a carefully regulated jet of air is blown through the coal. At the bottom of the producer, the carbon in the coal is burned to carbon dioxide:

$$\underset{\text{carbon}}{C} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{carbon dioxide}}{CO_2}$$

As this gas passes up through the incandescent coal above, it is reduced to carbon monoxide:

$$\underset{\text{carbon dioxide}}{CO_2} + \underset{\text{carbon}}{C} \longrightarrow \underset{\text{carbon monoxide}}{2\,CO}$$

This carbon monoxide, with some hydrogen and hydrocarbons, together with the nitrogen of the original air, constitute "producer gas."

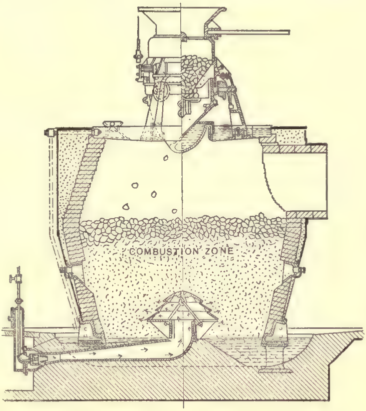


FIG. 113.—GAS PRODUCER.

About 6 % of steam is often mixed with the air in the blast. This steam increases the amount of combustible material in the gas, as it reacts with the coal to form carbon monoxide and hydrogen, both of high fuel value:

$$\underset{\text{water}}{H_2O} + \underset{\text{carbon}}{C} \longrightarrow \underset{\text{carbon monoxide}}{CO} + \underset{\text{hydrogen}}{H_2}$$

The difference between the action with steam and with air is that, in the case of the steam, there is no non-combustible gas, like nitrogen, remaining, and also the producer may be operated at a lower temperature.

When bituminous coal is used, the percentage of hydrocarbons is much higher than with hard (anthracite) coal, and the heating power of the gas and the efficiency of conversion of the coal into gas is higher. From 82 % to 87 %

of the energy contained in the original coal is left in the producer gas. This gas is used in the regular way in the gas engine. The application of producer gas and of waste gases from blast furnaces and coke ovens, have made practical the development of high power gas engines.

381. Combustion in the Engine. — The proportions of gas and air that give the best results in the engine range from 6 of air to 1 of gas, which gives about the highest pressure at the instant of combustion, to 8 of air to 1 of gas, which is the best working pressure under ordinary conditions, as the combustion continues through a larger portion of the stroke with the latter mixture. With a proper mixture of gas and air, the products of combustion are non-poisonous gases, which are exhausted into the atmosphere. The reactions of the oxygen of the air with the most important constituents of the gas (carbon monoxide, hydrogen, and marsh gas), are shown in the following equations:

$$\underset{\substack{\text{carbon}\\ \text{monoxide}}}{2\,CO} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{2\,CO_2}$$

$$\underset{\text{hydrogen}}{2\,H_2} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{water}}{2\,H_2O}$$

$$\underset{\text{methane}}{CH_4} + \underset{\text{oxygen}}{2\,O_2} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2} + \underset{\text{water}}{2\,H_2O}$$

382. Gasoline and Kerosene Engines. — The vapors of liquid fuels, such as gasoline and kerosene, are extensively used in internal-combustion engines. The automobile has brought the gasoline engine to a high degree of perfection. The gasoline engine differs from the gas engine only in the fact that gasoline vapor is used instead of gas. The gasoline is introduced in drops or a fine spray into the carburetor, which is a heated chamber where it is mixed with air and is vaporized. The gasoline engine, as employed in the aëroplane, represents a maximum of power with a minimum of space and weight.

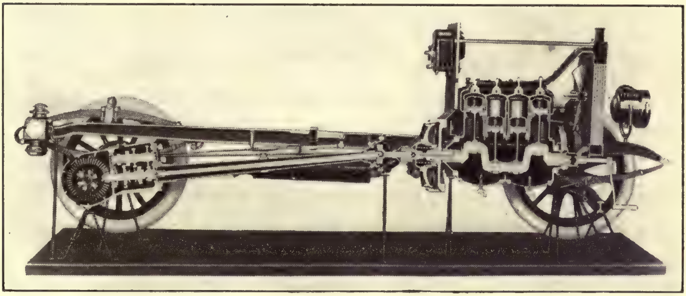


FIG. 114. — AUTOMOBILE ENGINE — 4-CYLINDER.

Kerosene oil is also used in engines similar in construction to the gas engine. It is usually introduced as a spray directly into the cylinder, whose walls, heated from the previous charge, vaporize the oil. The heat generated by the compression of the charge is sufficient to ignite it, so the electric spark is not necessary.

SUMMARY

The Gas Engine derives its power from the explosive combustion of a mixture of gas and air in the cylinder.

The combustible mixture is (*a*) introduced into the cylinder, (*b*) compressed, (*c*) ignited, and (*d*) the burned gases are driven out.

About six times as much air as gas is required for the most efficient operation of the gas engine.

In Gas Producers, a partial combustion of coal takes place, resulting in the formation of carbon monoxide. Steam is sometimes mixed with the air used in producers; in that case, hydrogen as well as carbon monoxide is produced. A ton of coal furnishes more energy when used with a gas producer and gas engine than when used with a boiler and steam engine.

Liquid Fuels may be used in internal combustion engines, by being first converted into a vapor or spray.

EXERCISES

1. Give an example, other than a gas engine, of energy directly produced by the burning of an explosive mixture.

2. During what fraction of the time that a gas engine is running is power being exerted on the flywheel?

3. What advantage has a four-cylinder automobile engine over a single-cylinder engine of the same power?

4. Write equations showing the formation of producer gas when a mixture of air and steam is used.

5. What advantages result from the use of bituminous rather than anthracite coal in a gas producer?

6. Write equations to show the composition of the exhaust from a gas engine, taking gas from a gas producer using steam and air.

7. What proportions of air and gas are most efficient in a gas engine? Why?

8. Why must liquid fuels be vaporized or converted into a spray before they are used in internal-combustion engines?

9. What results from feeding too much gasoline to an automobile engine?

10. Explain, with diagrams, the operation of a four-cycle engine.

CHAPTER XXXV

EXTRACTION OF METALS

383. Minerals and Ores. — A *mineral* is an inorganic substance of definite chemical composition found in the earth. A mass of any one mineral of sufficient extent to be an important source of an element is seldom found pure. The natural deposits from which the elements, especially the metals, are extracted are termed *ores*. An ore generally consists of a mineral containing the desired element, mixed with undesirable substances which must be eliminated during the process of extraction. To use a common illustration, large quantities of iron are obtained from the mineral hematite (ferric oxide). Hematite is commonly found mixed with sand and other substances which must be eliminated during the process of extracting the iron. The mixture of ferric oxide with other materials constitutes an important ore of iron.

384. Carbonates as Ores. — All common carbonates, with the exception of sodium carbonate and potassium carbonate, when heated, decompose before they melt, yielding carbon dioxide and a metallic oxide. Carbon dioxide, being a gas, escapes and leaves the non-volatile metallic oxide behind. Some of the metallic carbonates are important ores. In order to separate metals from them, they are frequently heated to convert them into oxides, which are subsequently reduced by heating with a reducing agent. For example, zinc oxide is obtained from zinc carbonate, iron oxide from iron carbonate, and copper oxide from copper carbonate.

When any one of these oxides is heated with carbon as a reducing agent, usually in the form of coke or charcoal, the carbon combines with the oxygen of the metallic oxide and leaves the metal behind. The two steps of the process may be carried on in one operation.

$$\underset{\substack{\text{zinc}\\ \text{carbonate}}}{ZnCO_3} \longrightarrow \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2} + \underset{\substack{\text{zinc}\\ \text{oxide}}}{ZnO}$$

$$\underset{\substack{\text{zinc}\\ \text{oxide}}}{ZnO} + \underset{\text{carbon}}{C} \longrightarrow \underset{\substack{\text{carbon}\\ \text{monoxide}}}{CO} + \underset{\text{zinc}}{Zn}$$

385. Sulphides as Ores. — When the ore is a sulphide, it is roasted, that is, heated in air to bring about some desired chemical change. If the metal contained in the ore does not form an oxide readily, or if its oxide is easily decomposed by heat, the metal may be obtained directly from the roasted ore. Mercury is obtained in this way from its principal ore, mercuric sulphide or cinnabar. When the mercuric sulphide is heated in contact with air, the combined sulphur is oxidized to sulphur dioxide, which escapes as a gas. The oxide of mercury does not appear because it is readily decomposed by heat. Mercury passes off as a vapor which is readily condensed, and is thus separated from the more volatile sulphur dioxide, and from the non-volatile constituents of the ore:

$$\underset{\substack{\text{mercuric}\\ \text{sulphide}}}{HgS} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{sulphur}\\ \text{dioxide}}}{SO_2} + \underset{\text{mercury}}{Hg}$$

In the case of metals whose sulphides oxidize readily, roasting is often employed to free the ore from the combined sulphur and to convert the metal into an oxide. The metallic oxide may be desired for commercial use, or it may be reduced in order to obtain a metal:

$$\underset{\substack{\text{zinc}\\\text{sulphide}}}{2\,\mathrm{ZnS}} + \underset{\text{oxygen}}{3\,\mathrm{O_2}} \longrightarrow \underset{\substack{\text{sulphur}\\\text{dioxide}}}{2\,\mathrm{SO_2}} + \underset{\substack{\text{zinc}\\\text{oxide}}}{2\,\mathrm{ZnO}}$$

$$\underset{\substack{\text{zinc}\\\text{oxide}}}{\mathrm{ZnO}} + \underset{\text{carbon}}{\mathrm{C}} \longrightarrow \underset{\substack{\text{carbon}\\\text{monoxide}}}{\mathrm{CO}} + \underset{\text{zinc}}{\mathrm{Zn}}$$

386. Use of Electricity. — Metals such as aluminum, sodium, potassium, magnesium, and calcium, whose oxides cannot be economically reduced, are obtained by electrolytic processes.

387. Aluminum is one of the metals prepared on a large scale by electrolysis. The process should be of interest to American boys on account of its invention by an American youth just out of college. Charles M. Hall was graduated from Oberlin College in 1885. He invented the process at present employed for the manufacture of aluminum in 1886, when he was in his twenty-second year. The form of apparatus employed has been perfected since that time, but the method remains fundamentally unchanged. The process invented in this country by Hall and that invented independently in France by Heroult are practically the same. What the invention of these men has meant commercially is shown by the fact that in 1889, just before the Hall process was placed on a commercial basis, aluminum sold for $4 a pound, while at present the price of aluminum is about 20 cents a pound in ingot form.

Bauxite, an ore containing from 50 % to 70 % of alumina (aluminum oxide), is the chief source of alumina. In refining the bauxite, advantage is taken of the fact that alumina forms with soda a compound known as sodium aluminate, Na_3AlO_3, which is soluble in water. The impurities in bauxite are insoluble or nearly so. The sodium aluminate formed by the action of soda with bauxite is separated from its impurities by filtering. The sodium aluminate in the filtrate is decomposed, the aluminum being thrown out of the solution as a hydrate. This hydrate is heated in a furnace for 48 hours at temperatures which gradually reach 1100° C. This drives off water from the hydrate and leaves it in the form of alumina ready to be used in the aluminum furnace.

Aluminum oxide is a very stable compound and cannot be reduced by heating with carbon. When heated with carbon in an electric furnace, aluminum carbide is obtained. Its fusion point is so high that the melting of alumina on a large scale is practically impossible. Since alumina is insoluble in water, some other solvent must be sought for the electrolytic bath.

Cryolite ($3\,NaF\,.\,AlF_3$) is a mineral having a low melting point, but, when melted, is a very poor conductor of electricity. Now, aluminum oxide is readily soluble in molten cryolite and the solution is a good conductor of electricity. On the passage of the current through the solution of alumina in molten cryolite, the aluminum oxide is decomposed, aluminum being liberated at the cathode and oxygen at the anode. Hall made use of such an electrolysis for the preparation of aluminum.

388. Commercial Extraction of Aluminum. — The apparatus (Fig. 115) employed for the commercial extraction of aluminum consists of an iron box, about 8 feet long, 4 feet wide, and 2 feet deep, lined with a thick layer of carbon which serves as the cathode. Carbon rods about 3 inches in diameter are used as anodes. About 40 carbon rods are used in one piece of apparatus.

An artificial mixture of fluorides, containing the fluorides of sodium, calcium, and aluminum, is placed in the apparatus and the carbon rods are jammed against the bottom of the apparatus. On the passage of the electric current, the rods become heated and the mixture of fluorides melts. The rods are then raised slightly from the bottom of the box and alumina is added. The aluminum oxide is decomposed, as described above, and the aluminum collects in the lower part of the box, from which it is drawn from time to time by removing a wooden plug from the taphole. The oxygen which appears at the carbon anodes oxidizes them so that the amount of carbon consumed about equals the weight of the aluminum obtained. A layer of coke is spread over the top of the molten mass, to prevent radiation and to protect the workman's eyes. The aluminum oxide is placed on the layer of coke and dries before it is stirred into the bath.

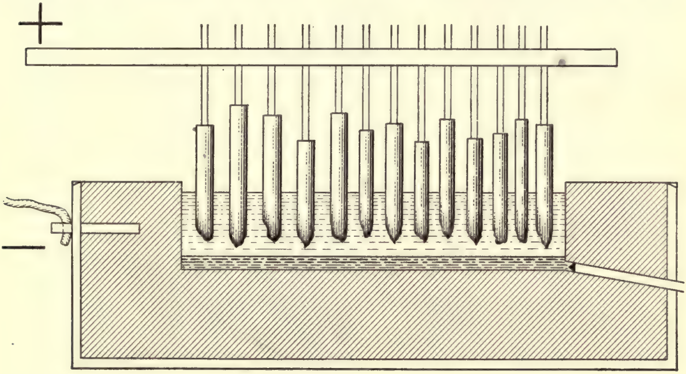


FIG. 115. — ELECTROLYTIC EXTRACTION OF ALUMINUM.

As the amount of alumina in solution decreases, the resistance of the bath increases. This fact is made use of to operate a signal which calls the attention of the operator to the fact that the bath needs attention. Alumina is added by stirring in some of that which has been drying on the coke. During the electrolysis the resistance of the
]]>

bath is sufficient to generate enough heat to keep the bath in a molten condition.

Aluminum is at present one of the common metals and is extensively employed for making cooking utensils, electric cables, and valuable alloys.

389. Thermit. — The fact that aluminum is a far more powerful reducing agent than carbon was discovered by Prof. Hans Goldschmidt of Essen. At present, the Goldschmidt Thermit Company is making practical use of this important discovery for the extraction of the formerly expensive metals manganese and chromium from their oxides, for the production of many valuable alloys, and for the production of molten iron at a temperature sufficiently high to weld broken parts of machinery and steel rails.

When a mixture of granulated aluminum and ferric oxide is ignited, the aluminum burns very rapidly and takes oxygen from the ferric oxide, reducing it to iron. The energy of the reaction is so great that a temperature of 3000° C. is produced. The use of another oxide, or of other oxides, in place of the ferric oxide makes possible the preparation of the metals manganese and chromium:

$$\underset{\substack{\text{manganese}\\\text{dioxide}}}{3\,MnO_2} + \underset{\text{aluminum}}{4\,Al} \longrightarrow \underset{\substack{\text{aluminum}\\\text{oxide}}}{2\,Al_2O_3} + \underset{\text{manganese}}{3\,Mn}$$

Valuable alloys, such as ferrotitanium, chromium-copper, and manganese-boron are prepared by the Thermit process.

Since the apparatus and the material necessary to weld together broken parts of large machines occupy little space and can be easily transported, the Thermit process has become of great value for making repairs in cases where the removal of the broken part would cause much delay and great expense. The Thermit process of welding is carried on essentially as follows:

A crucible shaped furnace (Figs. 116, 117) is charged with a mixture of granulated aluminum and ferric oxide, to which an alloy may be added to give the union the desired strength. On top of the charge is placed a small amount of an ignition mixture, consisting of magnesium powder mixed with barium peroxide. The pieces of the broken part are brought into alignment, enough metal is removed from the fractured ends to permit a free flow of liquid between the parts to be welded, a mold is built around the fracture, and the ends to be joined are heated by a gasoline blow-torch. The charged crucible is placed so that molten metal can be delivered from it into the mold, and the ignition mixture is lighted with a match. The heat generated by the burning ignition mix-

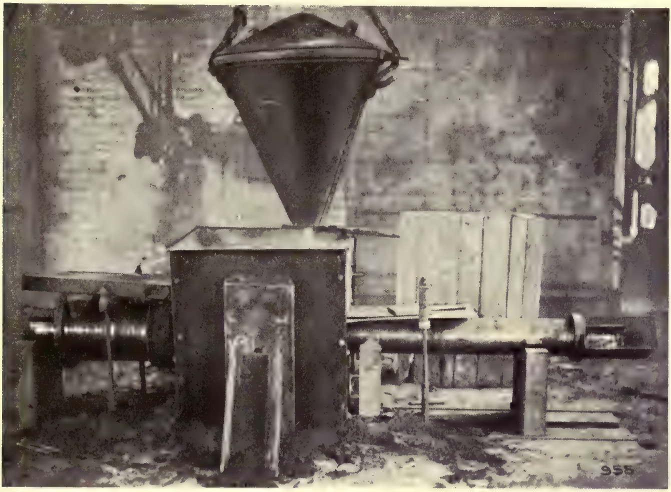


FIG. 116.—THERMIT CRUCIBLE FOR WELDING.

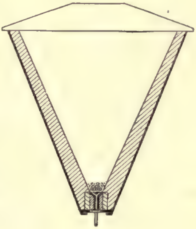


FIG. 117.

ture sets fire to the crucible charge. The aluminum in burning takes oxygen from the ferric oxide and leaves molten iron, heated to a temperature of 3000° C., on which floats aluminum oxide. The molten iron is then run into the mold surrounding the fracture. The extremely hot liquid iron flows between the surfaces to be joined, melts some of the metal and mingles with it, so that when the mass cools, the pieces of the broken part are united by metal as strong as that of which the machine is made. This process is one of the methods for autogenous welding (see Chapter XXXIII).

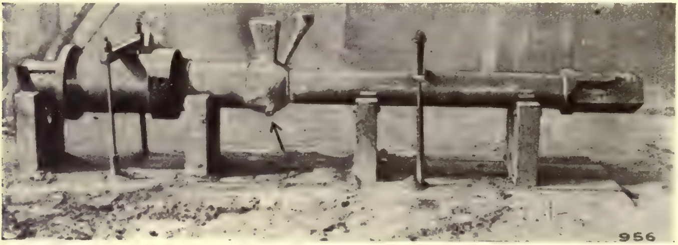


FIG. 118. — THERMIT WELDING.

390. Gold is sometimes found free in sand and in quartz rock. To separate the gold from such mixtures, the mass in which it occurs is pulverized by crushing, if necessary, and the gold extracted from the fine material by one of the following methods:

1st. When gold is mixed with sand, it is often separated by a process called *panning*, which consists in agitating the mixture in a pan-shaped vessel filled with water. The gold settles to the bottom and the impurities are poured off with the water.

2d. The free gold is *amalgamated*, that is, dissolved in mercury. The resulting amalgam is then mechanically purified, and the gold obtained by distilling off the mercury.

3d. The gold is dissolved in alkaline cyanide solutions in the presence of oxygen or an oxidizing agent, as shown by the equations:

$$\underset{\text{gold}}{2\,\mathrm{Au}} + \underset{\substack{\text{potassium}\\ \text{cyanide}}}{4\,\mathrm{KCN}} + \underset{\text{water}}{2\,\mathrm{H_2O}} + \underset{\text{oxygen}}{\mathrm{O_2}} \longrightarrow$$

$$\underset{\substack{\text{potassium}\\ \text{aurocyanide}}}{2\,\mathrm{KAu(CN)_2}} + \underset{\substack{\text{potassium}\\ \text{hydroxide}}}{2\,\mathrm{KOH}} + \underset{\substack{\text{hydrogen}\\ \text{peroxide}}}{\mathrm{H_2O_2}}$$

$$\underset{\text{gold}}{2\,\mathrm{Au}} + \underset{\substack{\text{potassium}\\ \text{cyanide}}}{4\,\mathrm{KCN}} + \underset{\substack{\text{hydrogen}\\ \text{peroxide}}}{\mathrm{H_2O_2}} \longrightarrow \underset{\substack{\text{potassium}\\ \text{aurocyanide}}}{2\,\mathrm{KAu(CN)_2}} + \underset{\substack{\text{potassium}\\ \text{hydroxide}}}{2\,\mathrm{KOH}}$$

From the potassium aurocyanide the gold may be precipitated by zinc, or by electrolysis.

$$\underset{\substack{\text{potassium}\\ \text{aurocyanide}}}{2\,\mathrm{KAu(CN)_2}} + \underset{\text{zinc}}{\mathrm{Zn}} \longrightarrow \underset{\substack{\text{potassium}\\ \text{zinc cyanide}}}{\mathrm{K_2Zn(CN)_4}} + \underset{\text{gold}}{2\,\mathrm{Au}}$$

4th. The pulverized ore containing the gold is treated with chlorine to form auric chloride, which is soluble. The solution of auric chloride may be treated with hydrogen sulphide to form the insoluble compound auric sulphide. The sulphide is then separated by filtration and decomposed by roasting.

$$\underset{\substack{\text{auric}\\ \text{chloride}}}{2\,\mathrm{AuCl_3}} + \underset{\substack{\text{hydrogen}\\ \text{sulphide}}}{3\,\mathrm{H_2S}} \longrightarrow \underset{\substack{\text{auric}\\ \text{sulphide}}}{\mathrm{Au_2S_3}} + \underset{\substack{\text{hydrogen}\\ \text{chloride}}}{6\,\mathrm{HCl}}$$

$$\underset{\substack{\text{auric}\\ \text{sulphide}}}{\mathrm{Au_2S_3}} + \underset{\text{oxygen}}{3\,\mathrm{O_2}} \longrightarrow \underset{\substack{\text{sulphur}\\ \text{dioxide}}}{3\,\mathrm{SO_2}} + \underset{\text{gold}}{2\,\mathrm{Au}}$$

391. Complex Ores. — Many ores are complex mixtures of minerals which require treatments far too complicated to be understood by the beginner.

392. Types of Furnaces. — Several types of furnaces are used in the extraction of metals. Among these, the blast furnace, the reverberatory furnace, the Bessemer converter, the open-hearth furnace, and the Goldschmidt or "Thermit" furnace are of great importance. The first four are described in detail in Chapter XL.

393. The Reverberatory Furnace (Fig. 119) is used in a large number of metallurgical operations. The fire grate is placed at one end of the furnace and the flame from the burning fuel passes just under the roof and over the furnace charge. In this way the carbon from the fuel is prevented from entering the charge. The heat from the burning gases reverberates back and forth between the roof and the charge. A reverberatory furnace can be used at will for the oxidation or the reduction of the heated material. If an excess of air is allowed to enter the furnace, so that free oxygen passes over the bed, oxidation takes place. If, on the other hand, an amount of air less than that required for the complete combustion of the fuel gases is allowed to enter the furnace, oxygen is taken from the charge, which is thus reduced.

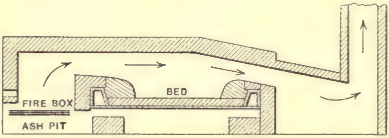


FIG. 119. — REVERBERATORY FURNACE.

394. Extraction of Lead. — Lead is frequently obtained from ores rich in the sulphide of lead (galena) by treatment in a reverberatory furnace. The lead sulphide is first heated in the presence of an excess of air (*roasted*), the ore being meanwhile stirred frequently. By this process a part of the lead sulphide is converted into lead oxide, according to the equation:

$$\underset{\substack{\text{lead}\\\text{sulphide}}}{2\,PbS} + \underset{\text{oxygen}}{3\,O_2} \longrightarrow \underset{\substack{\text{lead}\\\text{oxide}}}{2\,PbO} + \underset{\substack{\text{sulphur}\\\text{dioxide}}}{2\,SO_2}$$

Another portion of the lead sulphide is oxidized to lead sulphate, as shown by the equation:

$$\underset{\substack{\text{lead}\\\text{sulphide}}}{PbS} + \underset{\text{oxygen}}{2\,O_2} \longrightarrow \underset{\substack{\text{lead}\\\text{sulphate}}}{PbSO_4}$$

At the end of the roasting, a mixture of lead oxide, lead sulphate, and lead sulphide remains. The temperature of the furnace is then raised and the amount of oxygen entering the furnace is reduced. Under these conditions the lead sulphide takes oxygen from the lead oxide and lead sulphate, as shown by the equations:

$$\underset{\substack{\text{lead}\\\text{oxide}}}{2\,PbO} + \underset{\substack{\text{lead}\\\text{sulphide}}}{PbS} \longrightarrow \underset{\substack{\text{sulphur}\\\text{dioxide}}}{SO_2} + \underset{\text{lead}}{3\,Pb}$$

$$\underset{\substack{\text{lead}\\\text{sulphate}}}{PbSO_4} + \underset{\substack{\text{lead}\\\text{sulphide}}}{PbS} \longrightarrow \underset{\substack{\text{sulphur}\\\text{dioxide}}}{2\,SO_2} + \underset{\text{lead}}{2\,Pb}$$

This operation will be seen to be a process of reduction, in which lead sulphide is used as a reducing agent to remove oxygen from the mixture. As the lead separates, it runs down the sloping bed of the furnace and is removed. The process of oxidation and reduction are alternately repeated, and fine coal is added to complete the final reduction.

395. Extraction of Tin. — The extraction of tin from its chief ore, tin oxide, SnO_2 (cassiterite), is often carried on in a reverberatory furnace. The tin oxide is mixed with coal, which serves as the reducing agent.

$$\underset{\text{stannic oxide}}{SnO_2} + \underset{\text{carbon}}{2\,C} \longrightarrow \underset{\text{carbon monoxide}}{2\,CO} + \underset{\text{tin}}{Sn}$$

The impure tin thus obtained is slowly heated in another reverberatory furnace so that the pure tin, which melts at a lower temperature, runs off, leaving behind a less fusible alloy of tin with iron, arsenic, etc.

SUMMARY

A Mineral is an inorganic substance of definite composition found in the earth.

An Ore is a more or less pure mineral from which a useful element is extracted.

All Common Carbonates, with the exception of the carbonates of sodium and potassium, are decomposed by heat before they melt. Use is made of this fact in the preparation of calcium oxide from calcium carbonate and in the conversion of several carbonates into oxides preparatory to reduction by carbon.

Sulphides. — Mercuric sulphide when roasted in air is converted into sulphur dioxide and mercury vapor. Many sulphides are converted into oxides when heated in air and the oxide is then reduced.

Electrolysis. — Sodium, potassium, magnesium, calcium, and aluminum are obtained by electrolysis. Aluminum is obtained by the decomposition of aluminum oxide which has been dissolved in a mixture of molten fluorides.

Gold is separated from impurities by panning, or by dissolving it in mercury, or in a solution of potassium cyanide, or chlorine.

Thermit is a mixture of granulated aluminum with one or more metallic oxides. It is used in smelting manganese and chromium oxides, in the preparation of various alloys, and to weld broken castings and other iron and steel articles.

A Reverberatory Furnace has the fire grate at one end of the furnace and the flames pass above the furnace charge. It receives its name from the fact that the heat reverberates between the roof of the furnace and the charge. The reverberatory furnace is used in the smelting of certain ores of tin, lead, and copper, and in the refining of iron and copper.

EXERCISES

1. What is a mineral? How does a mineral differ from an ore?

2. Name an important iron mineral and an important iron ore.

3. Make a general statement concerning the decomposition of carbonates by heat.

4. Name three carbonates contained in important ores.

5. How could zinc be obtained from zinc carbonate?

6. Mention three sulphides which are important sources of metals.

7. Why is not mercuric oxide obtained when mercuric sulphide is roasted?

8. What processes would you use to obtain copper from copper sulphide?

9. Name three elements which are obtained by electrolytic processes.

10. Give a description of the Hall process for the manufacture of aluminum.

11. In the Hall process, what use is made of the molten fluorides? Of the aluminum oxide? What becomes of the oxygen liberated during the process?

12. What is the reducing agent most frequently used in the reduction of metallic oxides?

13. How are manganese and chromium obtained from their oxides?

14. What reduction takes place when a mixture of finely divided aluminum and ferric oxide are ignited in a crucible? Give the equation.

15. Describe the Thermit welding process.

16. Define an amalgam. How is gold regained from gold amalgam?

17. What would happen if a gold ring were placed on some mercury?

18. Describe briefly a process by which gold is extracted from an ore.

19. How can lead be obtained from galena?

20. Name an important ore of tin and describe a method for extracting tin from it.

CHAPTER XXXVI

ELECTRIC FURNACES

396. The Conversion of Electricity into Heat Energy has so many applications in modern chemical operations that only a few of the more important ones can be mentioned in a book of this size. Two extensive industries of American origin are the manufacture of calcium carbide and of carborundum.

397. Calcium Carbide. — In 1892, Thomas L. Wilson, while experimenting at Spray, North Carolina, tried to produce calcium by the reduction of calcium oxide by carbon in an electric furnace. His experiment was unsuccessful so far as the production of calcium was concerned, but from it arose an unexpected industry of great importance. It is said that Wilson, on making an examination of the contents of the furnace at the close of the experiment, saw that he had not produced calcium, and ordered the contents of the furnace to be discarded. The workmen threw some of the material into a near-by stream and, much to the surprise of those present, a gas was generated. The gas was found

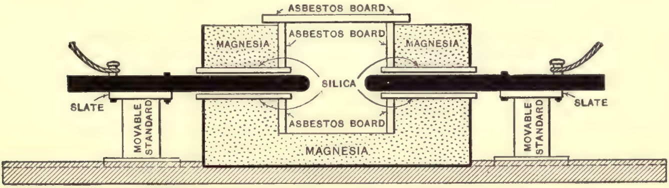

ASBESTOS BOARD
MAGNESIA
ASBESTOS BOARD
MAGNESIA
SILICA
SLATE
MOVABLE STANDARD
ASBESTOS BOARD
MAGNESIA
MOVABLE STANDARD
SLATE

FIG. 120. — LABORATORY ELECTRIC FURNACE.

to burn readily, producing a very smoky flame. Thus was started the manufacture of calcium carbide on a large scale. This instance serves to illustrate the many cases in which scientific investigation has not reached its goal, but has resulted in an unexpected discovery of great value. Wilson did not know the name of the compound which he had accidentally discovered, and did not dream of the important part it was to play in our present everyday life. A consideration of the importance of calcium carbide for use in the generation of acetylene (§§ 99, 119) and for the production of calcium cyanamide (§ 509) will give the reader some idea of the enormous value of Wilson's discovery.

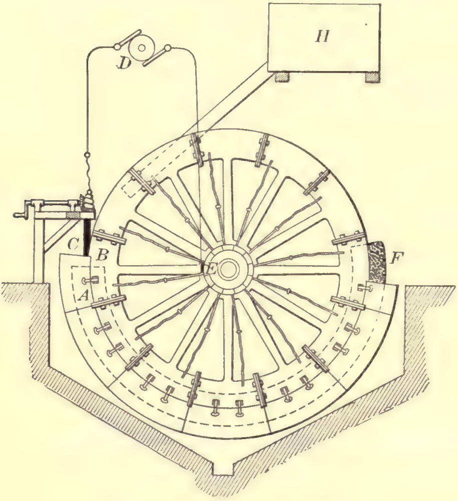


FIG. 121.—ROTARY CARBIDE FURNACE.

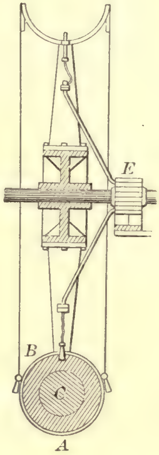


FIG. 122.

Calcium carbide can be readily prepared on a small scale in any laboratory provided with a current suitable for operating a small electric furnace such as is represented in Fig. 120. Calcium oxide and a good grade of carbon, such as that used for electric light carbons, are finely ground and thoroughly mixed. On heating the mixture for some time in the arc of the furnace, a reaction takes place by which calcium carbide and carbon monoxide are produced according to the equation:

$$\underset{\text{calcium oxide}}{\mathrm{CaO}} + \underset{\text{carbon}}{3\,\mathrm{C}} \longrightarrow \underset{\text{carbon monoxide}}{\mathrm{CO}} + \underset{\text{calcium carbide}}{\mathrm{CaC_2}}$$

Calcium carbide is at present prepared in a furnace similar to that illustrated in Figs. 121, 122. The furnace consists of an iron wheel (*B*) composed of insulated segments, to which can be attached removable cover plates (*A*). The mixture of coke and lime is delivered from the bin (*H*) to the hollow space between the grooved wheel and the cover. One terminal of the dynamo (*D*) is connected to the graphite electrode (*C*), which is in contact with the mixture; the other terminal is connected to the segment of the wheel containing the mixture, by means of a sliding contact on the commutator (*E*). As the mixture is converted into carbide, the wheel is rotated, covers attached where needed, and fresh mixture supplied, making the process continuous. The finished carbide is removed at the opposite side of the wheel at (*F*).

398. Carborundum or Silicon Carbide. — E. G. Acheson, in 1891, while trying to impregnate clay with carbon under the influence of electric heat, obtained a small quantity of a beautiful, crystalline substance which was found to rival the diamond in hardness. The usefulness of this new substance as an abrasive occurred to Acheson. Believing the newly discovered substance to be derived from carbon and clay, he gave it the name of carborundum. Later investigations showed that it was formed by a reaction between the carbon and the sand (silicon dioxide) mixed with the clay. Although it is silicon carbide, SiC, it still retains the trade name carborundum. Carborundum is to-day the most important abrasive on the market.

Carborundum is prepared by heating a mixture of sand, coke, salt, and sawdust in an electric furnace, the construction of which is represented in Fig. 123. Under the influence of the high temperature produced by the electric current, the sand (silicon dioxide) and coke (carbon) react as shown by the equation:

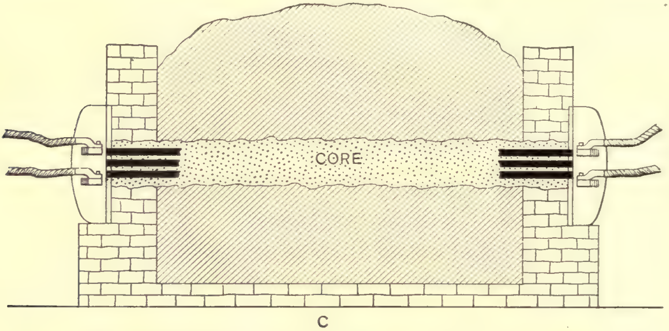


FIG. 123. — CARBORUNDUM FURNACE — SECTIONAL.

$$\underset{\text{silicon dioxide}}{SiO_2} + \underset{\text{carbon}}{3\,C} \longrightarrow \underset{\text{carbon monoxide}}{2\,CO} + \underset{\text{silicon carbide}}{SiC}$$

The sawdust is used because when heated it liberates gases which keep the mass porous so that the carbon monoxide can escape readily and burn in numerous small flames at the surface of the mixture (Fig. 124).

Carborundum is so hard that the lumps taken from the furnace cannot be ground. They are, however, brittle and are readily crushed beneath heavy stone wheels. The coarser portions of the crushed material are separated into grains of a definite size by means of sieves, while the finer portions are sorted by *elutriation*, that is, by the rate at which they sink in a stream of running water, the larger particles being, of course, the first to settle.

Carborundum, in a great variety of sizes, is sold in bulk. It is glued to cloth, thus making a substance resembling emery cloth, or sandpaper. It is also mixed with clay-like substances, and the mixture is molded and baked in a kiln. In this way, various shaped stones suitable for all sorts of sharpening and grinding work are made.

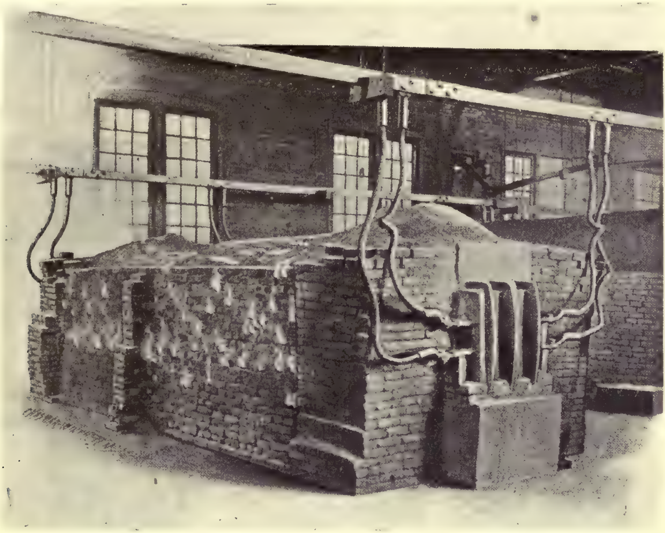
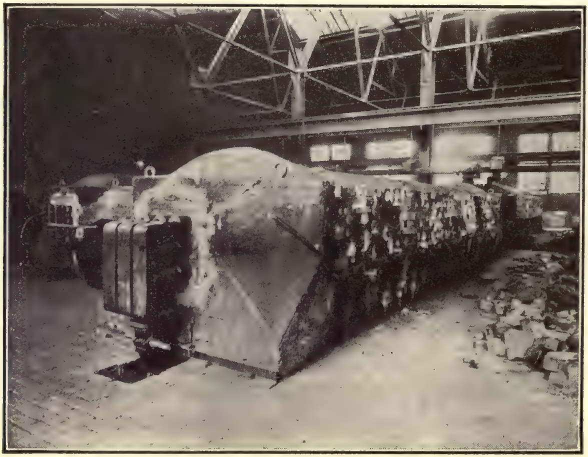


FIG. 124. — ELECTRIC CARBORUNDUM FURNACE.

399. Artificial Graphite. — The use of the electric furnace for the manufacture of carborundum led to the discovery of a method for the manufacture of artificial graphite. Graphite was formed in the hottest part of the carborundum furnace, that is, next to the core. The high temperature decomposed the silicon carbide in contact with the core, the silicon being volatilized and the carbon deposited in the form of graphite. A long series of experiments convinced Acheson that varieties of graphite differing greatly in luster and unctuousness can be produced in the electric furnace, and that, while it is possible to make graphite from pure carbon, the unctuous varieties of graphite can be obtained from carbon only when it is mixed with mineral matter such as silica, iron oxide, etc. The impurities probably first react with the carbon to form carbides which subsequently decompose.



Copyright by the *International Acheson Graphite Co.*

FIG. 125. — ELECTRIC GRAPHITE FURNACE.

The pulverized coal of the Pennsylvania anthracite coal mines when mixed with sand and heated in the electric furnace (Fig. 125) yields the purest quality of unctuous graphite. Much of the artificial graphite is made from such material.

Artificial graphite is extensively used in the manufacture of electrodes and in the preparation of lubricants. Natural graphite is used for the purposes just mentioned, for the making of crucibles in which metals are to be melted, for the manufacture of the leads of lead pencils, in stove and shoe blacking, and for lubricants and boiler compounds.

400. Deflocculated Graphite. — By treating finely ground amorphous or non-crystalline graphite with a solution of tannin or any one of several other organic substances, the graphite may be converted into particles sufficiently fine to pass through filter paper and to remain in suspension when mixed with water or with oil. Acheson calls this form of graphite "deflocculated graphite." Deflocculated graphite mixed with water has the trade name of "Aquadag," and deflocculated graphite diffused in oil has been given the name "Oildag." Aquadag is used as an aid in metal cutting and Oildag is one of the most valuable lubricants on the market. By mixing a cheap oil with graphite a product can be obtained which is equal to a high-grade oil for use as a lubricant.

401. Lead Pencils. — In the manufacture of leads for pencils, the graphite is first separated from the mica and sand with which it is found mixed in the natural deposits. As pure graphite is too soft for the general requirements of a pencil, it is mixed with fine clay free from particles of grit. By varying the amounts of clay and graphite, mixtures of various hardness can be obtained and from these are made the leads for the great variety of pencils on the market. The mixture of clay and graphite is ground in water between millstones, passed between rolls and through a mixer, and then squeezed through a die to form a rod having the shape of the lead of the pencil to be made. The leads after being dried are subjected to a temperature of about 1100° C. The heat toughens the lead so it is ready to be placed in the wood of the pencil.

402. Carbon Disulphide (CS_2) is a very volatile liquid which burns in a manner similar to gasoline. The application of the electric furnace to its manufacture is due to another American, Edward R. Taylor. The construction of the furnace used is shown in Fig 126. As no air can be permitted to enter the furnace, the electrodes are fixed and are prevented from wearing away by delivering pieces of carbon over their ends. Part of the heat developed between the electrodes passes to the walls of the furnace, where it is used to melt sulphur. Within the furnace the sulphur vapor combines directly with the carbon as shown by the equation:

$$\underset{\text{carbon}}{C} + \underset{\text{sulphur}}{2\,S} \longrightarrow \underset{\text{carbon disulphide}}{CS_2}$$

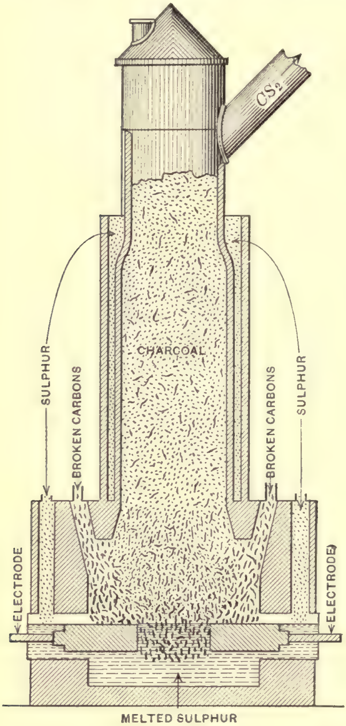


FIG. 126.—ELECTRIC FURNACE FOR MAKING CARBON DISULPHIDE.

Carbon disulphide is used to destroy insects of various kinds and burrowing animals, such as moles, woodchucks, etc.; as a solvent for rubber and sulphur, and lately large quantities have been consumed in the manufacture of artificial silk.

403. Electric Smelting and Refining. — Recently the electric furnace has been introduced as a source of heat for the smelting of ores. A simple form of a furnace designed for the smelting of tin is shown in Fig. 127.

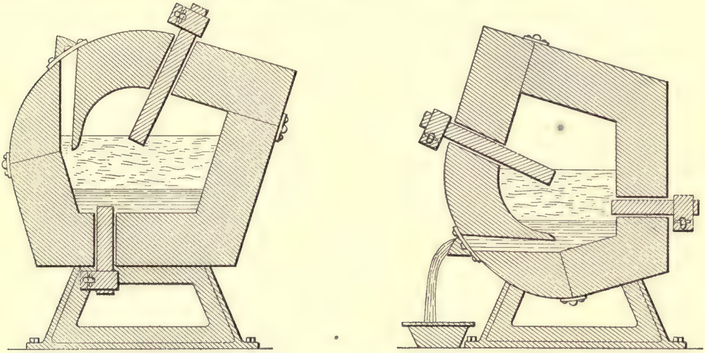


FIG. 127.—FURNACE FOR SMELTING TIN.

A furnace invented by Heroult, who has already been mentioned in connection with Hall's process for the production of aluminum (§ 387), is used in this country for the production of high-grade steel. An idea of the working of this furnace may be gained from Figs. 128, 129 and from the following description. The furnace is made in two parts, the bed and the roof, which are so constructed that they may be readily separated. It is mounted so that it can be tipped to permit the charge to run out. The bed of the furnace consists of a steel shell lined with a layer of fire brick, on which is a layer of dolomite (calcium magnesium carbonate). The cover is made of iron and is lined with fire brick. In the large Heroult furnaces, capable of treating 15 tons of steel at a time, 3 electrodes are used. These are made of rods of Acheson graphite, 8 inches in diameter. The rods are joined so as to form one rod 144 inches long. A bundle of 3 of the long rods constitutes one electrode. As iron readily combines with carbon at the temperature of the furnace, the electrodes are not permitted to touch the steel. They dip into the slag which floats on the steel. The slag is said to consist of magnetite (Fe_3O_4) and a basic flux, the former being used as an oxidizing agent and the latter to combine with the sulphur and phosphorus oxides obtained by the oxidation of the sulphur and phosphorus in the impure steel or iron. The electrodes are automatically regulated so that their ends are about 18 inches above the steel. They are separated so that the current arcs from the electrode to the slag, and from the slag to the steel underneath. The current then leaves the

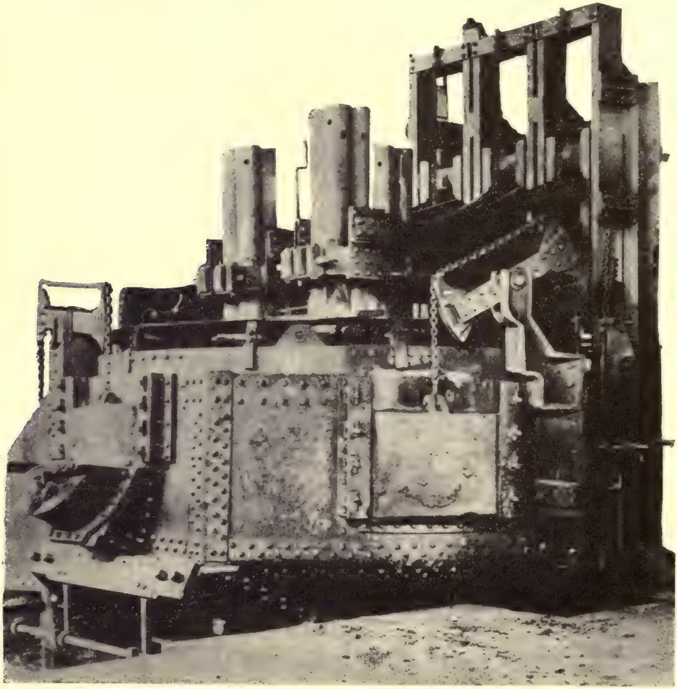


FIG. 128.—HEROULT ELECTRIC FURNACE FOR STEEL.

furnace by arcing from the steel to the slag and from the slag to the electrode by which it returns to the dynamo. An alternating current is employed.

The Heroult furnace has been proved to be of great value for removing undesirable elements, sulphur and phosphorus, from a low-grade Bessemer steel, thus producing a high grade steel. In general, the furnace provides an economical means for the refining of steel.

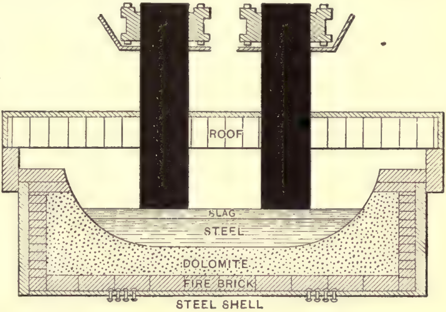


FIG. 129. — HEROULT FURNACE — SECTIONAL.

SUMMARY

Calcium Carbide, CaC_2, is made by heating in an electric furnace ground coke and lime which have been thoroughly mixed. The temperature of the furnace is about 3000° C. Calcium carbide is extensively used for the production of acetylene, and increasing quantities of it are being employed in the production of calcium cyanamide.

Carborundum, silicon carbide, SiC, is made by heating a mixture of coke, sand, sawdust, and salt in an electric furnace. It closely approximates the diamond in hardness and is extensively employed as an abrasive.

Artificial Graphite is prepared by heating impure carbon in an electric furnace. The unctuousness of the graphite depends on the amount of silica, ferric iron, and other mineral matter mixed with the carbon. Much artificial graphite is made by heating a mixture of silica and anthracite culm. Artificial graphite has many uses, two of the more important being the manufacture of electrodes and lubricants.

The Lead of Lead Pencils consists of various mixtures of graphite and clay, finely ground in water and thoroughly incorporated, then molded, dried, and subjected to a high temperature to harden them. The greater the percentage of clay in the mixture the harder the lead.

Carbon Disulphide is prepared by heating carbon and sulphur in an electric furnace which is so arranged that air cannot enter it. Carbon disulphide is used as an insecticide, as a solvent for rubber, and in the manufacture of artificial silk.

The Smelting and Refining of Metals by the energy derived from the electric current is rapidly increasing.

EXERCISES

1. Briefly tell how calcium carbide came to be manufactured on a commercial scale.

2. From what is calcium carbide made? Equation?

3. Mention important uses of calcium carbide.

4. What is carborundum? How is it made? Equation?

5. How is the carborundum that comes from the furnace converted into material sufficiently fine for use as an abrasive?

6. How are carborundum wheels made?

7. What led to the discovery of artificial graphite?

8. Upon what does the unctuousness of graphite seem to depend?

9. What chemical changes probably take place during the formation of an unctuous graphite?

10. Mention an important source of the carbon used in the manufacture of artificial graphite.

11. What are some of the uses of artificial graphite?

12. Briefly describe the making of the lead of a lead pencil.

13. How is carbon disulphide made?

14. Why is it necessary to prevent air from entering the carbon disulphide furnace when it is in operation?

15. Why is great care taken to prevent the consumption of the electrodes of a carbon disulphide furnace? How is this accomplished?

16. For what purposes is carbon disulphide used?

17. Account for the rapid increase in the use of the electric current for metallurgical operations.

18. Make a sectional drawing of the Heroult furnace for the refining of steel.

19. Trace the path of the current through the Heroult furnace.

20. What becomes of the impurities in the unrefined steel in an electric furnace?

21. A few years ago many predicted that the open-hearth furnace would entirely take the place of the Bessemer converter. How is the electric furnace likely to modify this prediction?

CHAPTER XXXVII

ELECTROCHEMISTRY

404. Development of Electrochemistry. — Every improvement in the generation of electric currents has been followed by a great extension of the uses of electricity. The growth of water-power plants for generating electricity, which began in this country in the last decade of the nineteenth century, has been accompanied by the development of electrochemical processes for the manufacture of materials formerly prepared in other ways; by the application of electrical methods to the extraction and refining of metals; and by the separation of elements and the production of new compounds, which electrical processes alone can effect. A few of the more important relations between electricity and chemical action will be discussed in this chapter.

405. Conduction of Electricity. — There are two classes of substances which act as conductors for the electric current. The first class includes *metallic conductors*, such as copper, aluminum, brass, and iron, and some solid non-metallic substances, of which carbon is the most important. The passage of a current through these conductors is not accompanied by any change in the conductor, other than the development of a certain amount of heat.

Members of the second class of conductors are known as *electrolytes*. The most important electrolytes are water solutions of acids, bases, and salts. Some melted compounds also act as electrolytes. The passage of a current through an electrolyte is accompanied by the liberation of two different substances. One of these appears at the terminal where the current enters the solution, known as the *anode*, or + electrode, and the other at the terminal at which the current leaves, called the *cathode*, or − electrode.

For example, if carbon electrodes are placed in a solution of hydrogen chloride and a current passed, chlorine gas is liberated at the anode, and hydrogen at the cathode. If sodium chloride is used instead of hydrogen chloride, chlorine is liberated at the anode and sodium hydroxide is found in the solution surrounding the cathode. Before attempting to explain this result it will be necessary to state the theory of electrolytic dissociation.

406. Dissociation Theory. — According to this theory, when an electrolyte is dissolved in water, a portion at least of its molecules break up into two parts, one charged with positive electricity and the other with an equal amount of negative electricity. These charged portions of the molecule are called respectively positive and negative *ions*. Thus, when sodium chloride is dissolved in water, an equal amount of positive sodium ions and of negative chlorine ions are produced. This may be indicated by the equation:

$$\underset{\substack{\text{sodium chloride}\\ \text{molecule}}}{\mathrm{NaCl}} \leftrightarrows \underset{\substack{\text{sodium}\\ \text{ion}}}{\mathrm{Na}^+} + \underset{\substack{\text{chlorine}\\ \text{ion}}}{\mathrm{Cl}^-}$$

Hydrochloric acid dissociates in solution according to the equation:

$$\underset{\substack{\text{hydrochloric acid}\\ \text{molecule}}}{\mathrm{HCl}} \leftrightarrows \underset{\substack{\text{hydrogen}\\ \text{ion}}}{\mathrm{H}^+} + \underset{\substack{\text{chlorine}\\ \text{ion}}}{\mathrm{Cl}^-}$$

Sodium hydroxide dissociates in solution as follows:

$$\underset{\substack{\text{sodium hydroxide}\\ \text{molecule}}}{\mathrm{NaOH}} \leftrightarrows \underset{\substack{\text{sodium}\\ \text{ion}}}{\mathrm{Na}^+} + \underset{\substack{\text{hydroxyl}\\ \text{ion}}}{\mathrm{OH}^-}$$

It will be noted in these typical examples of the dissociation of a salt, an acid, and a base, that the hydrogen ion and the metallic ion are positive, and that the non-metallic ions are negative.

In a solution of copper sulphate there are copper ions and sulphate ions:

$$\underset{\text{copper sulphate molecule}}{CuSO_4} \rightleftarrows \underset{\text{copper ion}}{Cu^{++}} + \underset{\text{sulphate ion}}{SO_4^{--}}$$

A double charge is indicated here on each ion, as the number of charges which an ion carries is the same as the number expressing its valence (§ 50). Molecules of the dissolved substance in an electrolyte, then, dissociate, *on dissolving*, into positive metallic ions and negative non-metallic ions. Hydrogen, in acids and acid salts, acts as a metallic ion; in bases it is a part of the complex non-metallic ion OH^-. The only important complex positive ion is NH_4^+, produced by the dissociation of ammonium hydroxide and the ammonium salts.

The proportion of the molecules dissociated at a particular time in a given electrolyte depends on the nature of the dissolved substance, the degree of dilution of the solution, and the temperature. Water is the only important solvent in which any considerable amount of dissociation takes place. Many soluble substances, particularly organic compounds such as sugar, alcohol, and glycerin, do not dissociate on dissolving. Such solutions are known as *non-electrolytes* and are non-conductors of electricity. Pure water is a very poor conductor, and therefore its molecules are only slightly dissociated.

407. Explanation of Electrolysis. — On the basis of the theory just stated the electrolysis of sodium chloride is easily explained. When the electrodes are dipped into the solution and the circuit closed, the Na^+ ions, which have been moving about at random in the solution, are immediately repelled by the positive electrode and attracted by the negative electrode, since like electric charges always repel and unlike charges attract. For the same reason the Cl^- ions begin to move toward the positive electrode. As soon as an ion reaches the electrode, the opposite charges on ion and electrode neutralize each other. The chlorine ion, losing its charge, becomes a chlorine atom; these unite in pairs to form molecules. When a sufficiently large number of such molecules have collected at the anode, they will escape from the solution as a bubble of chlorine gas. In a similar way the sodium ions lose their charge at the cathode and become sodium atoms. These do not, however, unite to form pieces of metallic sodium, since they react with the water to form sodium hydroxide:

$$\underset{\textbf{sodium}}{2\,Na} + \underset{\textbf{water}}{2\,H_2O} \longrightarrow \underset{\textbf{sodium hydroxide}}{2\,NaOH} + \underset{\textbf{hydrogen}}{H_2}$$

Bubbles of hydrogen, therefore, will escape at the cathode. The sodium *ion* did not react with the water, because the presence of the electric charge gives the ion chemical properties differing from those of the atom.

The electrolysis of water, described on page 3, may now be explained. It was there stated that sulphuric acid might be added to make the water a conductor. Considering the action first as an electrolysis of sulphuric acid, the acid dissociates on dissolving in the water into hydrogen ions and sulphate ions:

$$\underset{\substack{\textbf{sulphuric acid}\\ \textbf{molecule}}}{H_2SO_4} \rightleftarrows \underset{\substack{\textbf{hydrogen}\\ \textbf{ion}}}{H^+} + \underset{\substack{\textbf{hydrogen}\\ \textbf{ion}}}{H^+} + \underset{\substack{\textbf{sulphate}\\ \textbf{ion}}}{SO_4^{--}}$$

As the current passes, the ions lose their charges at the electrodes. At the cathode hydrogen ions change to hydrogen atoms which unite to form molecules of hydrogen. At the anode, SO_4^{--} changes to SO_4, which immediately reacts with the water as follows:

$$\underset{\substack{\text{sulphate}\\ \text{radical}}}{SO_4} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} + \underset{\text{oxygen}}{O}$$

Thus a new molecule of sulphuric acid has been produced in place of the one originally dissociated and an atom of oxygen has been liberated. The oxygen atoms liberated at the anode unite to form oxygen molecules, which escape as a gas. The entire reaction therefore may be considered as equivalent to that shown by the equation:

$$\underset{\text{water}}{2H_2O} \longrightarrow \underset{\text{hydrogen}}{2H_2} + \underset{\text{oxygen}}{O_2}$$

408. Commercial Electrolysis. — In the commercial production of hydrogen and oxygen by electrolysis, a solution of caustic potash, KOH, is used as the electrolyte. The outer iron tank (Fig. 131) serves as the negative electrode and a perforated inner tank made of iron of special composition is the positive electrode. These electrodes are separated by means of a diaphragm of asbestos (*H*), which permits the charged ions to pass freely, but prevents the mixing of the bubbles of liberated gas. A hydraulic joint (*G*) also prevents the mixing of the liberated gases, and pressure equalizers on top (*C*) deliver the gases at constant pressure through pipes (*A*, *B*) to the gas holders or to compression pumps, for compressing it into cylinders.

The first action in the electrolysis is the dissociation of the potassium hydroxide when it dissolves:

$$\underset{\substack{\text{potassium hydroxide}\\ \text{molecule}}}{KOH} \rightleftarrows \underset{\substack{\text{potassium}\\ \text{ion}}}{K^+} + \underset{\substack{\text{hydroxyl}\\ \text{ion}}}{OH^-}$$

When the potassium ion reaches the negative electrode, it loses its charge, becomes a potassium atom, and reacts with the water of the solution, forming potassium hydroxide again and liberating hydrogen:

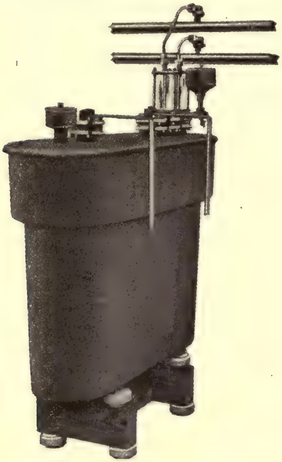


FIG. 130. — ELECTROLYTIC GENERATOR FOR HYDROGEN AND OXYGEN.

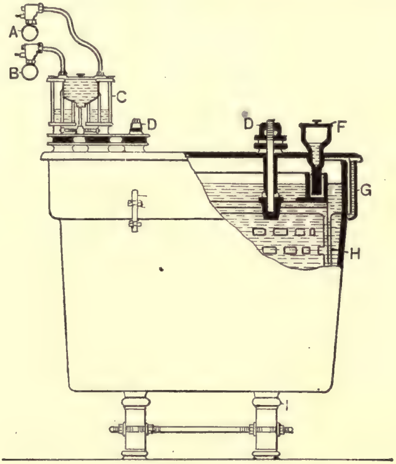


FIG. 131. — ELECTROLYTIC GENERATOR — SECTIONAL. D, D, ELECTRIC TERMINALS. F, FUNNEL FOR FILLING.

$$\underset{\text{potassium}}{2\,K} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{potassium hydroxide}}{2\,KOH} + \underset{\text{hydrogen}}{H_2}$$

The hydroxyl ions, when they lose their charges, react with each other, forming water and liberating oxygen:

$$\underset{\text{hydroxyl}}{OH} + \underset{\text{hydroxyl}}{OH} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\text{oxygen}}{O}$$

It will be seen that the net result of these reactions is the removal of one molecule of water from the solution and the liberation of two atoms of hydrogen and one atom of oxygen. So it is only the water in the cell which needs to be renewed and not the potassium hydroxide.

The hydrogen produced by this process is over 99% pure and the oxygen more than 98%. Where electric current is obtained cheaply the cost of this process of producing oxygen is much lower than that of the potassium chlorate process usually employed. In many cases, the hydrogen produced can also be utilized in the preparation of substitutes for lard, an industry of increasing importance (§ 210).

409. Explanation of Neutralization. — The dissociation theory offers an explanation for the chemical reactions in which solutions of acids, bases, and salts take part. In terms of this theory, an acid may be defined as a compound whose water solution contains hydrogen ions; a base, as a compound whose solution contains hydroxyl (OH^-) ions; a neutral salt, as a compound whose water solution contains positive ions from a base and negative ions from an acid. It has already been seen (§ 28) that water and a salt are the products of neutralization. Now water is only very slightly dissociated in solution and salts are very highly dissociated. Therefore if a solution containing H^+ ions (an acid) is mixed with a solution containing OH^- ions (a base), there will be a decided tendency for each pair of these ions to unite to form a molecule of water:

$$\underset{\text{hydrogen ion}}{H^+} + \underset{\text{hydroxyl ion}}{OH^-} \longrightarrow \underset{\text{water molecule}}{HOH}$$

If an equation for neutralization is written so as to show the ions into which the acid and the base dissociate, it will be seen that the simplest reaction possible will be the union of the positive H^+ ion from one compound with the negative OH^- ion from the other, since the unlike charges of these ions will cause them to attract each other. The reaction between hydrochloric acid and sodium hydroxide solutions will serve as an example:

$$\underset{\substack{\text{hydrogen}\\ \text{ion}}}{H^+} + \underset{\substack{\text{chlorine}\\ \text{ion}}}{Cl^-} + \underset{\substack{\text{sodium}\\ \text{ion}}}{Na^+} + \underset{\substack{\text{hydroxyl}\\ \text{ion}}}{OH^-} \longrightarrow \underset{\substack{\text{water}\\ \text{molecule}}}{HOH} + \underset{\substack{\text{sodium}\\ \text{ion}}}{Na^+} + \underset{\substack{\text{chlorine}\\ \text{ion}}}{Cl^-}$$

The only permanent change which has taken place is the uniting of the ions H^+ and OH^- to form water. The ion Na^+ and Cl^- remain in solution and only unite to form NaCl on evaporation. *Neutralization*, then, is essentially the uniting of the H^+ ions of an acid with the OH^- ions of a base to form undissociated water. The equations for other neutralizations will show that the formation of undissociated water is the feature common to them all. For example:

$$\underset{\substack{\text{hydrogen}\\ \text{ion}}}{H^+} + \underset{\substack{\text{nitrate}\\ \text{ion}}}{NO_3^-} + \underset{\substack{\text{potas-}\\ \text{sium}\\ \text{ion}}}{K^+} + \underset{\substack{\text{hydroxyl}\\ \text{ion}}}{OH^-} \longrightarrow \underset{\substack{\text{water}\\ \text{molecule}}}{HOH} + \underset{\substack{\text{potas-}\\ \text{sium}\\ \text{ion}}}{K^+} + \underset{\substack{\text{nitrate}\\ \text{ion}}}{NO_3^-}$$

$$\underset{\substack{\text{hydrogen}\\ \text{ions}}}{2(H^+)} + \underset{\substack{\text{sulphate}\\ \text{ion}}}{SO_4^{--}} + \underset{\substack{\text{sodium}\\ \text{ions}}}{2(Na^+)} + \underset{\substack{\text{hydroxyl}\\ \text{ions}}}{2(OH^-)} \longrightarrow$$

$$\underset{\substack{\text{water}\\ \text{molecules}}}{2\,HOH} + \underset{\substack{\text{sodium}\\ \text{ions}}}{2(Na^+)} + \underset{\substack{\text{sulphate}\\ \text{ion}}}{SO_4^{--}}$$

410. Other Reactions between Electrolytes. — Many reactions take place because of the union of positive ions from one compound with negative ions from another to form a compound which is undissociated, because it is an insoluble solid. The use of silver nitrate as a test for the presence of a chloride, that is, of the Cl^- ion, is an example of a reaction due to the formation of an insoluble compound. Suppose a solution of sodium chloride (NaCl) is mixed with a solution of silver nitrate ($AgNO_3$). The following reaction will take place:

$$\underset{\substack{\text{sodium}\\\text{ion}}}{Na^+} + \underset{\substack{\text{chloride}\\\text{ion}}}{Cl^-} + \underset{\substack{\text{silver}\\\text{ion}}}{Ag^+} + \underset{\substack{\text{nitrate}\\\text{ion}}}{NO_3^-} \longrightarrow \underset{\substack{\text{silver chloride}\\\text{molecule}}}{AgCl} + \underset{\substack{\text{sodium}\\\text{ion}}}{Na^+} + \underset{\substack{\text{nitrate}\\\text{ion}}}{NO_3^-}$$

This reaction proceeds to completion because the ions Ag^+ and Cl^- unite permanently to form molecules of AgCl, which will not again dissociate, because they are *insoluble.* It is evident that any soluble chloride would behave in a way similar to sodium chloride, because its solution would contain Cl^- ions. As all nitrates are soluble, their solutions will always contain positive metallic ions and NO_3^- ions, as such.

A reaction also completes itself when a combination of ions produces a substance, volatile under the existing conditions. The ions on uniting leave the solution as undissociated molecules of the volatile substance.

411. Primary Cells. — The production of electricity in galvanic batteries, or primary cells, is the result of the conversion of chemical energy into electrical energy. A cell consisting of a zinc plate and a copper plate, immersed in dilute sulphuric acid, is called a *simple cell* (Fig. 132). When zinc reacts with dilute sulphuric acid, the following action takes place:

$$\underset{\substack{\text{zinc}\\\text{atom}}}{Zn} + \underset{\substack{\text{hydrogen}\\\text{ions}}}{2(H^+)} + \underset{\substack{\text{sulphate}\\\text{ion}}}{SO_4^{--}} \longrightarrow \underset{\substack{\text{zinc}\\\text{ion}}}{Zn^{++}} + \underset{\substack{\text{sulphate}\\\text{ion}}}{SO_4^{--}} + \underset{\substack{\text{hydrogen}\\\text{molecule}}}{H_2}$$

The same reaction takes place between the zinc plate and the acid in the simple cell. The zinc plate, before immersion in the acid, shows no trace of either positive or negative electricity, that is, the positive and the negative electricity in the plate are just equal and so balance each other. As the zinc ions carry their positive charge with them from the zinc plate when they enter the solution, they leave the plate charged with negative electricity. Copper does not react chemically with dilute sulphuric acid. As the Zn^{++} ions repel the H^+ ions of that part of the acid which has not yet come in contact with the zinc plate, these H^+ ions will move away from the zinc toward the copper plate, constantly repelling the H^+ ions which are in front of them. The result is that the H^+ ions which are near the copper plate will come in contact with that plate. They then give up their positive charge to the copper plate and unite to form molecules of hydrogen. The copper plate is now charged positively and the zinc plate negatively. If the plates are connected by a wire or other conductor, the positive and negative charges will pass through the wire to neutralize each other, and this constitutes a current of electricity.

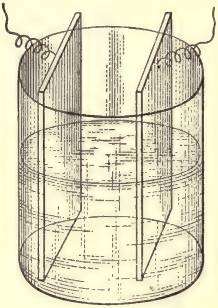


FIG. 132.

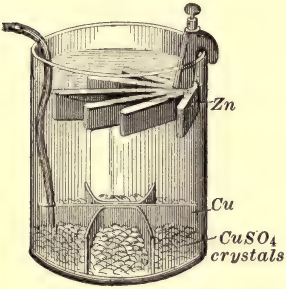


FIG. 133. — GRAVITY CELL.

Most of the molecules of hydrogen liberated at the copper cathode of the simple cell will unite to form bubbles of hydrogen gas, which escape into the air. Some of the hydrogen, however, adheres to the copper plate, and so tends to check the action or *polarize* the cell. In the *Daniell cell* polarization is prevented by surrounding the copper with a solution of copper sulphate. This solution is kept separate from the sulphuric acid by placing the zinc and sulphuric acid in a porous cup, while the copper is immersed in the copper sulphate solution contained in the outer vessel. In the *gravity cell* (Fig. 133) the two liquids are separated by the difference in their specific gravity. In both cells, Cu^{++} ions will be repelled to the copper plate instead of H^+ ions, and so no polarization will take place as long as the supply of copper sulphate is maintained. The "bluestone" cells, frequently used on telegraph lines, are gravity cells.

412. Sal Ammoniac Cells. — Another cell, which is more widely used than either the simple or the Daniell cell, is the *sal ammoniac* cell. The electrodes of this cell are zinc and carbon, and the electrolyte is a solution of ammonium chloride (sal ammoniac). The reaction which takes place is:

$$\underset{\substack{\text{zinc}\\ \text{atom}}}{\mathrm{Zn}} + \underset{\substack{\text{ammonium}\\ \text{ions}}}{2(\mathrm{NH_4^+})} + \underset{\substack{\text{chlorine}\\ \text{ions}}}{2(\mathrm{Cl^-})} \longrightarrow$$

$$\underset{\substack{\text{zinc}\\ \text{ion}}}{\mathrm{Zn^{++}}} + \underset{\substack{\text{chlorine}\\ \text{ions}}}{2(\mathrm{Cl^-})} + \underset{\substack{\text{hydrogen}\\ \text{molecule}}}{\mathrm{H_2}} + \underset{\substack{\text{ammonia}\\ \text{molecules}}}{2\,\mathrm{NH_3}}$$

This equation represents the final result of the action. It is altogether probable that the NH_4^+ ions are repelled by the Zn^{++} ions as these enter the solution, and that the following reaction takes place at the cathode:

$$\underset{\substack{\text{ammonium}\\ \text{ions}}}{2(\mathrm{NH_4^+})} \longrightarrow \underset{\substack{\text{ammonia}\\ \text{molecules}}}{2\,\mathrm{NH_3}} + \underset{\substack{\text{hydrogen}\\ \text{molecule}}}{\mathrm{H_2}}$$

A small portion of the ammonia escapes, but the greater part dissolves in the water. As in the case of the simple cell, hydrogen may accumulate on the surface of the cathode and so polarize the cell.

The cell just described is called the *carbon cylinder* cell. When manganese dioxide is present as a depolarizer, the cell is called the *Leclanché* cell (Fig. 134). The manganese dioxide, a black powder, is usually mixed with granulated carbon to increase the conductivity, and the mixture is packed around the carbon of the cell. A slow reaction goes on in the presence of hydrogen, by which the hydrogen is oxidized to water:

$$\underset{\text{manganese dioxide}}{2\,MnO_2} + \underset{\text{hydrogen}}{H_2} \longrightarrow \underset{\text{manganese trioxide}}{Mn_2O_3} + \underset{\text{water}}{H_2O}$$

As this reaction proceeds slowly, the cell is only suitable for intermittent uses, such as ringing door bells.

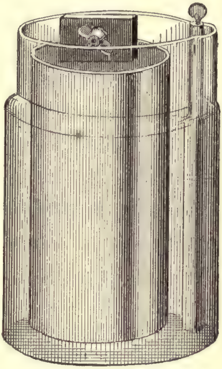


FIG. 134. — LECLANCHÉ CELL.

In recent years, the Leclanché cell has been largely replaced by the "dry" cell (Fig. 135). The zinc of the dry cell is in the form of a can, which serves as a container for the other parts. The zinc can (Z) is lined with absorbent paper, such as blotting paper, which is saturated with sal ammoniac. The carbon rod (C) is placed in the center of the cell and the space between it and the can is filled with a mixture of granulated manganese dioxide and graphite (E), thoroughly wet with sal ammoniac, and sometimes with other chemicals. The completed cell is sealed as shown at (P) to prevent the evaporation of the liquid. It is evident that the dry cell is simply a modification of the Leclanché cell. The dry cell is more compact and, as it has no liquid to spill, is more convenient

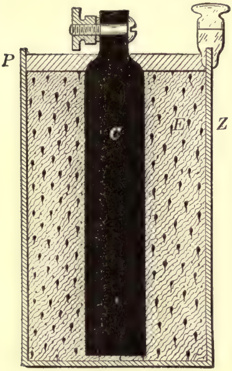


FIG. 135. — DRY CELL — SECTIONAL.

than the Leclanché cell, particularly where it must be carried in various positions, as in the ignition battery of an automobile. When a dry cell fails to act further, on account of the exhaustion of the electrolyte, it can be replaced cheaply, or it can be made to serve some time longer by punching holes through the zinc and placing the whole cell in a jar containing sal ammoniac solution.

413. Storage Cells. — Zinc, which is the positive plate of most important primary cells, is used up in the production of current, and the frequent replacement of the zinc makes these cells an expensive source of current, when much is required. In the secondary or *storage* cells the positive plate is a compound which gives up one of its elements to the electrolyte while the cell is furnishing current (discharging), and later has this element restored to it by passing a current from another source through the cell (charging).

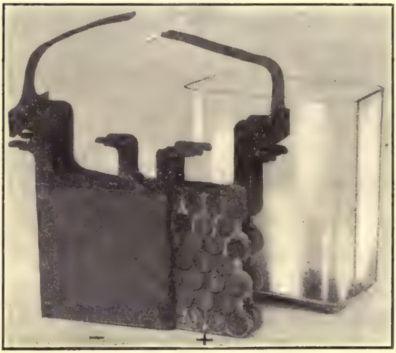


Fig. 136. — Chloride Accumulator Storage Battery, showing Negative and Positive Plates partly Separated, with Containing Jar Behind.

The *lead* storage battery is the most familiar type (Fig. 136). In a common commercial form of this battery, the positive plate consists of a framework or grid of lead, in the spaces of which is packed lead peroxide (PbO_2). The negative plate is another grid of lead, with its pockets packed with finely divided or *spongy* lead. The electrolyte is dilute sulphuric acid. The probable chemical reaction that takes place when the cell is furnishing current (discharging) is:

$$\underset{\substack{\text{lead}\\\text{plate}}}{\mathrm{Pb}} + \underset{\substack{\text{lead oxide}\\\text{plate}}}{\mathrm{PbO_2}} + \underset{\substack{\text{sulphuric acid}\\\text{electrolyte}}}{2\,\mathrm{H_2SO_4}} \longrightarrow \underset{\substack{\text{lead sulphate}\\\text{both plates}}}{2\,\mathrm{PbSO_4}} + \underset{\text{water}}{2\,\mathrm{H_2O}}$$

That is, each of the plates tends to become coated on the surface with lead sulphate. As this action proceeds, the electromotive force of the cell remains practically constant for a considerable time, and then gradually diminishes, because the two plates are becoming alike.

The cell is then *charged*, by connecting it to some other electric generator and allowing a current to pass. This current causes electrolysis and the final result is the reversal of the reaction given above, so that the equation for charging is:

$$\underset{\substack{\text{lead sulphate}\\\text{both plates}}}{2\,\mathrm{PbSO_4}} + \underset{\text{water}}{2\,\mathrm{H_2O}} \longrightarrow \underset{\substack{\text{lead}\\\text{plate}}}{\mathrm{Pb}} + \underset{\substack{\text{lead oxide}\\\text{plate}}}{\mathrm{PbO_2}} + \underset{\substack{\text{sulphuric acid}\\\text{electrolyte}}}{2\,\mathrm{H_2SO_4}}$$

Charging and discharging can be repeated a large number of times before the gradual disintegration of the plates makes it necessary to replace them. As a considerable amount of gas passes off during the process of charging, it is necessary to add water frequently and sulphuric acid occasionally. Some of the well-known commercial forms of this cell are the "Chloride Accumulator" and the "Exide" cells.

The weight of the lead storage battery and the mechanical weakness of its plates has considerably limited its use. The *Edison* storage battery is much lighter and stronger for the same capacity. Both

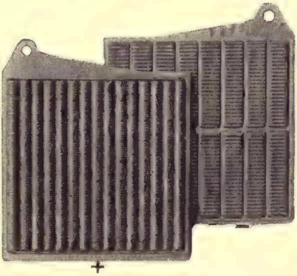


FIG. 137. — PLATES OF THE EDISON STORAGE BATTERY.

plates (Fig. 137) are of nickel-plated steel, with the active material contained in perforated pockets. In the positive plate, the active material is nickel peroxide and in the negative plate it is finely divided iron. The electrolyte is a solution of caustic potash. During discharge, the iron is oxidized and the nickel peroxide is partly reduced. The reaction is reversed in charging. At the positive plate, the equation is:

$$\underset{\substack{\text{nickel}\\\text{peroxide}}}{NiO_2} + \underset{\substack{\text{potassium}\\\text{ions}}}{2(K^+)} + \underset{\text{water}}{H_2O} \underset{\textit{charging}}{\overset{\textit{discharging}}{\rightleftarrows}} \underset{\substack{\text{nickel}\\\text{oxide}}}{NiO} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{2\,KOH}$$

The arrow shows in which direction the reaction is proceeding during the charging and the discharging of the cell. At the negative plate the reaction is:

$$\underset{\text{iron}}{Fe} + \underset{\substack{\text{hydroxyl}\\\text{ions}}}{2(OH^-)} \underset{\textit{charging}}{\overset{\textit{discharging}}{\rightleftarrows}} \underset{\substack{\text{iron}\\\text{oxide}}}{FeO} + \underset{\text{water}}{H_2O}$$

In both of these cells, during discharge, chemical energy is being converted into electrical energy; this chemical energy must be restored to the cell during the process of charging. Not all of the electrical energy used in charging the cell is converted into chemical energy: part of it goes into heat, which is dissipated. It is well to remember, therefore, that it takes longer to charge a storage cell than it does to discharge it, the rate of current flow being the same in both cases. This limits the full use of a given cell or set of cells to less than twelve hours out of twenty-four.

414. Electroplating, or the electrical deposition of a coating of an expensive metal on a cheaper one, is one of the most important applications of electrolysis (Fig. 138). The process of copper plating may be taken as a typical example. The anode is a plate of copper, the cathode is the article to be plated, and the electrolyte a solution of some copper salt, as copper sulphate. When current is supplied to the electroplating cell, the Cu^{++} ions in the solution travel toward the cathode, lose their charges, and the metallic copper is deposited on the cathode, as was explained in connection with the Daniell cell (§ 411). At the anode, fresh Cu^{++} ions are constantly entering the solution to take the place of those deposited on the plated article. Thus a solution of constant concentration is maintained. The rate at which the current passes must be carefully regulated, as upon this depends the fineness of the deposit and its adherence to the object being plated. For gold or silver plating, gold or silver anodes (Fig. 138, *a*) are used, and the electrolyte (*b*) is gold or silver cyanide, as the case may be. Plated tableware is made in this way. Other metals may be plated with brass, by employing a brass anode and a solution containing a mixture of copper and zinc salts in the proper proportion.

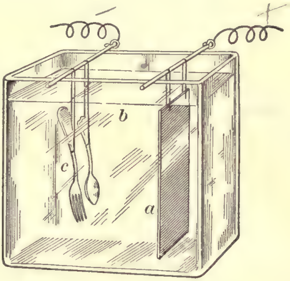
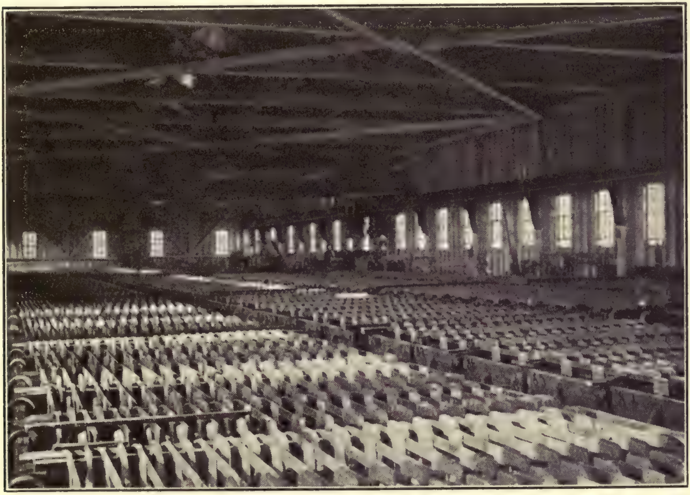


Fig. 138. — Silver Plating.

415. Electrotyping. — Any object may be electroplated if it is first given a conducting surface. This fact is utilized in preparing the plates from which books are printed. Lead type would quickly become dull if used to print thousands of copies. So an impression of the type of the page is made in wax and the surface coated with finely powdered graphite. This coated wax surface is then made the cathode of a copper plating bath and a current is sent through the bath, until a plating is obtained which is thick enough to retain its shape when removed. The wax is carefully melted away, leaving a thin sheet of copper, which is exactly like the original page of type. Melted lead or other easily fusible metal is poured into the back of the copper plate to give it strength, and the *electrotype*, as it is called, is mounted on a wooden block and is ready for use in the press. The entire process just described is called *electrotyping*. The electrotype plates may be used for thousands of impressions, and the type originally used for making them may be utilized again for other pages.

As every detail of the mold is reproduced in a properly made electrotype, this process makes possible the reproduction in metal of any object of suitable size. A careful mold of the object is made and electrotyped, and then the electrotype is filled with some suitable material to give it strength. Metal-coated clay statuettes and "silver deposit" glass vases are made by an electroplating process similar to electrotyping, in that the object is first given a conducting coating and then electroplated.

416. Refining of Metals. — Another important application of the electroplating process is in the refining of metals. The salts of different metals require different electromotive forces for their electrolysis. If, for example, the anode of a copper plating bath consists of an alloy of copper with other metals, the electromotive force applied to the bath may be so adjusted that only the copper will be transferred by the current to the cathode, while the other metals fall to the bottom of the cell. This process is actually employed as the final step in the refining of copper (Fig. 139). After the copper has been refined as far as possible by other processes, it is cast into plates. These are then made the anodes in a copper sulphate bath, the cathodes being pure copper. As the current passes, electrolytic copper of nearly 100 % purity is deposited on the cathode plates. Sometimes pure cathode plates are not used, but the impure plates are so arranged that copper from the front of one plate is deposited on the back of the next.



By courtesy of *The Scientific American.*

FIG. 139. — TANK HOUSE FOR ELECTROLYTIC COPPER REFINING.

The same principle is applied to the separation of gold and silver from each other. The alloy is made the anode plate in a solution of silver nitrate. The cathode is a silver plate, and the electromotive force is so adjusted that only the silver is deposited. To retain the gold as the anode plate disintegrates, the anode is surrounded with a canvas bag.

417. Gold and Silver Plating. — When silver salts are electrolyzed, the silver forms a crystalline coating on the cathode. The granular structure of such a coating makes it unsuitable for use in silver plating. If, however, a solution containing a mixture of potassium silver cyanide and potassium cyanide is used as an electrolyte, a coherent layer of silver is deposited on the cathode. Such a solution is, consequently, suitable for silver plating.

The changes which take place during this process of plating with silver are much more complex than those mentioned in the case of copper plating. Potassium silver cyanide, when dissolved in water, dissociates according to the equation :

$$\underset{\substack{\text{potassium silver cyanide}\\\text{molecule}}}{KAg(CN)_2} \quad \rightleftarrows \quad \underset{\text{potassium ion}}{K^+} \quad + \quad \underset{\text{silver cyanide ion}}{Ag(CN)_2^-}$$

On the passage of the current, the potassium liberated at the cathode immediately reacts with the potassium silver cyanide in the solution replacing the silver, which is deposited at the cathode :

$$\underset{\text{potassium silver cyanide}}{KAg(CN)_2} \quad + \quad \underset{\text{potassium}}{K} \quad \longrightarrow \quad \underset{\text{potassium cyanide}}{2\,KCN} \quad + \quad \underset{\text{silver}}{Ag}$$

At the anode the $Ag(CN)_2^-$ ions, on losing their charge, dissolve silver sufficient to form silver cyanide :

$$\underset{\text{silver cyanide radical}}{Ag(CN)_2} \quad + \quad \underset{\text{silver}}{Ag} \quad \longrightarrow \quad \underset{\text{silver cyanide molecules}}{2\,AgCN}$$

The silver cyanide unites with the free potassium cyanide in the solution and potassium silver cyanide is formed. To obtain good results, it is necessary to stir the bath during the operation of plating.

When potassium gold cyanide and potassium copper cyanide are used in electrolytic baths, changes similar to those just described take place. The best deposits of copper on iron are obtained by the cyanide process.

SUMMARY

Electrolytes are solutions in which the dissolved substance dissociates into positively and negatively charged ions, on dissolving. The passage of a current through an electrolyte is accompanied by the liberation of hydrogen or a metal at the cathode (− electrode), and a non-metal or non-metallic radical at the anode (+ electrode).

Non-Electrolytes are solutions in which no dissociation takes place on dissolving.

Electrolysis is the permanent decomposition of an electrolyte by the passage of a current through it. When ions lose their charge at the electrodes, they may react with the water or with the electrodes, as they then become simply atoms or groups of atoms.

An Acid, on dissolving, yields positive hydrogen ions. **A Base**, on dissolving, yields negative hydroxyl ions.

Neutralization consists in the union of the hydrogen ions from the acid with the hydroxyl ions from the base to form *undissociated water*. When the solution containing the remaining ions is evaporated, the residue is a *salt*.

A Precipitate will be formed when two electrolytes are mixed, provided the positive ions of one electrolyte can unite with the negative ions of the other to form an insoluble compound.

A Simple Voltaic Cell consists of a zinc plate and a copper plate immersed in dilute sulphuric acid. It converts chemical energy into electrical energy.

The Polarization of a cell is due to the collection of hydrogen bubbles at the cathode. **A Depolarizer** is a substance used to prevent this action.

The Daniell Cell has its copper plate immersed in copper sulphate solution to prevent polarization.

The Leclanché Cell has carbon and zinc electrodes; the electrolyte is ammonium chloride and the depolarizer is manganese dioxide. **The Dry Cell** is a modification of the Leclanché cell.

The Lead Storage Cell has electrodes of lead and lead peroxide. The electrolyte is dilute sulphuric acid. In discharging, both plates become covered with lead sulphate. They are restored to their original condition by passing a current through the cell (charging).

The Edison Storage Cell uses nickel peroxide and iron, with caustic soda as the electrolyte.

Objects are Electroplated by making them cathodes in an electrolytic bath, of which the anode is composed of the plating metal and the electrolyte is a salt of that metal.

In Electrotyping, a mold of the object to be copied is covered with graphite and plated with a shell of copper thick enough to retain its form when detached.

Some Metals are Refined by making them anodes in an electrolytic bath, with a cathode made of the pure metal and a salt of the metal as the electrolyte.

EXERCISES

1. How does the conduction of an electric current through a copper wire differ from that through salt water?

2. Explain clearly the meaning of the following terms: anode; cathode; ion; electrolyte; depolarizer.

3. State, with equations, what takes place when:
   (*a*) a few drops of nitric acid are poured into a beaker of water;
   (*b*) a few pieces of caustic potash are dropped into another beaker of water;
   (*c*) the contents of the two beakers are mixed.

4. Write the symbols of the ions formed, indicating the proper number of charges, when the following compounds are

dissolved in water: $Cu(NO_3)_2$; HBr; Na_2CO_3; $ZnSO_4$; NH_4OH; $NaHSO_4$.

5. Barium choride ($BaCl_2$) is soluble in water. Barium sulphate ($BaSO_4$) is insoluble. Devise a test for the SO_4^+ ion based on these facts.

6. Describe two litmus tests, stating for what ion each test is used.

7. Make a sketch of the apparatus for the electrolysis of a solution of sulphuric acid. Describe and explain the action.

8. Make a comparative table of the simple, Daniell, and Leclanché cells under the following headings: Name; positive plate; negative plate; electrolyte; depolarizer; chemical reaction.

9. Explain the depolarization of the Daniell and of the Leclanché cell.

10. Lead sulphate is a non-conductor of electricity. What would be the effect on a storage cell of continuing the discharge until the plates were entirely covered with lead sulphate?

11. Explain the advantage of an Edison storage cell, as compared with a Daniell cell.

12. Make a diagram of a copper plating cell, marking the electrodes and indicating the direction of the current.

13. Describe an electrical method of separating the silver of a piece of sterling silver (§ 183) from the metal alloyed with it.

14. What is electrolytic copper? How is it produced?

15. State what would happen during the passage of a current through a solution of sodium sulphate.

16. Could metallic sodium be produced by the electrolysis of a water solution of one of its salts? Explain.

17. How could you give a plaster cast a surface layer of copper?

18. How would you gold plate the inside of a silver cup?

CHAPTER XXXVIII

CORROSION OF METALS

NATURE OF CORROSION

418. Surface Change on Metals. — When freed from surface deposit by polishing, all metals present a highly lustrous appearance which is so characteristic that it is spoken of as "metallic luster." In the case of most metals, owing to chemical action by constituents of the air, this surface remains unchanged for only a short time. The quickness of the change is most noticeable with very active metals like sodium and potassium, in which cases the luster lasts but a few seconds. Less active metals change more slowly and the very inactive ones like gold and platinum do not change even after long periods of time. Between the two extremes lie the common metals, iron, zinc, lead, copper, which corrode easily, and silver, nickel, and aluminum, which are less subject to change.

419. Constituents of the Air Active in Causing Corrosion. — Oxygen is ordinarily regarded as the substance in the air responsible for the change, for the reason that the corroded matter is largely composed of oxide of the metal. It is probably true, however, that oxygen is not the sole cause of the action in the majority of cases. Moisture, carbon dioxide, and, in the vicinity of cities or large manufacturing plants, gaseous sulphur compounds formed from burning coal and gas, play an important part in the corrosion.

Considering first the case of *iron*, the most useful and, unfortunately, the most easily corroded of all common metals, experiments show that:

(1) iron does not rust in pure dry oxygen,

(2) iron does not rust in the presence of air and water if carbon dioxide is absolutely removed (except when the temperature is above 22° C. and the same water remains in contact with the iron for some time),

(3) acid vapors hasten the corrosion of iron, and

(4) bases retard the corrosion.

These observations make probable the conclusion that under ordinary conditions the corrosion of iron is *started* by the combined action of carbon dioxide and water, that is, by carbonic acid:

$$\underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2} \longrightarrow \underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_3}$$

The products of this first action are ferrous carbonate, $FeCO_3$, and hydrogen:

$$\underset{\text{iron}}{Fe} + \underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_3} \longrightarrow \underset{\substack{\text{ferrous}\\\text{carbonate}}}{FeCO_3} + \underset{\text{hydrogen}}{H_2}$$

All ferrous compounds will change into ferric compounds if they are in contact with air (oxygen) and water. The substance formed will be ferric hydroxide, $Fe(OH)_3$, if no free acid is present. Hence the initial corroding action is immediately followed by one represented in the following equation:

$$\underset{\substack{\text{ferrous}\\\text{carbonate}}}{4\,FeCO_3} + \underset{\text{water}}{6\,H_2O} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{ferric}\\\text{hydroxide}}}{4\,Fe(OH)_3} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{4\,CO_2}$$

The carbon dioxide which started the action is thus again set free and begins anew the initial action. The ferric hydroxide does not remain unchanged, but, by loss of water, is partly converted into the oxide, Fe_2O_3:

$$\underset{\substack{\text{ferric}\\\text{hydroxide}}}{2\,Fe(OH)_3} \longrightarrow \underset{\substack{\text{ferric}\\\text{oxide}}}{Fe_2O_3} + \underset{\text{water}}{3\,H_2O}$$

All these conclusions agree with an additional experimental observation, that iron rust is composed of ferric oxide, some unchanged ferric hydroxide, and traces of ferrous carbonate.

420. Corrosion of Other Metals. — The corrosion of other common metals is a far less serious matter than that of iron. In so far, however, as it does occur, it is also true that oxygen is probably not the sole cause of the change. In the case of silver, the corroded matter is largely sulphide, caused by the action of gaseous sulphur compounds of the air; the coating formed on copper may include copper sulphide, cuprous oxide, cupric oxide, and basic carbonate of copper. The last named of these substances is the one which gives to exposed copper the beautiful green color that it sometimes shows. On lead we find an analogous mixture of compounds, and such is the case with zinc. In all these cases the composition of the surface deposit will vary with the conditions.

PREVENTION OF CORROSION

421. Self-Protective Metals. — In a sense, all the common metals except iron are self-protective against corrosion. This is true because the deposit, when once formed, acts like a paint and prevents action by atmospheric agents. Lead used on the roofs of cathedrals built in the Middle Ages, on being scratched, shows only a thin surface deposit with the bright metal underneath. Copper rainspouts and cornice work of buildings are usually not painted, but are allowed to form their own protective coatings by corrosion. In the case of zinc, the corrosion proceeds somewhat more rapidly. Tin, nickel, and aluminum remain almost free from action, except that aluminum used for electric transmission lines shows a coating that is not well understood.

422. Iron Rust a Catalytic Agent for its Own Production. — As is well known, the rusting of iron proceeds very rapidly where it has once started. To preserve metal where this has happened is a very difficult matter, and is scarcely possible by any means, without first removing the existing deposit. It appears, therefore, that iron rust is a catalytic agent for the production of iron rust. The explanation of this fact is not definitely known, but one belief is that an electrolytic action is set up like that which occurs in batteries. The rust of iron acts as a cathode of the cell, the unchanged iron as an anode, and carbon dioxide and water, together forming carbonic acid, make the active solution. Currents of electricity circulate through the particles of rust, particles of unchanged metal, and the solution, with the result that iron, like the zinc of the cell, is dissolved, and ferric oxide and ferric hydroxide are eventually formed. In this way it is possible for the iron to be rusted through and through in a comparatively short space of time.

FIG. 140. — CORROSION OF IRON.

This fact makes a great deal of trouble in using the metal, and makes the permanency of iron structures a doubtful matter. It is practically always necessary to protect the metal with some coating. Unfortunately, no thoroughly satisfactory substance for this purpose has been discovered.

423. Protecting Iron by Deposits of Other Metals. — Iron can be protected reasonably well by covering it with a thin layer of another metal which is either free from corrosion, or self-protective against corrosion. One method of accomplishing this result is to *dip* the thoroughly cleaned iron into the melted metal. Either tin or zinc is used for the purpose. Tin does not protect against corrosion nearly so well as zinc, but, since this latter metal readily forms poisonous compounds, tin must be applied where the article is to serve as a food container or cooking utensil. Zinc does much better where the iron is used in making pails or troughs, or where it is to be used for building purposes. Iron that has been covered with tin is spoken of as "tin ware"; that which has been covered with zinc is called "galvanized" iron.

Another method of applying a coating of one metal to another is found in the use of the electric current as explained in § 414. By means of electrolysis, nickel is deposited on an iron object by making it the cathode in an electrolytic cell containing a solution of nickel ammonium sulphate. When definite conditions are established, a very good protective coating is secured if the iron has first been covered in a similar manner with a thin coating of copper. Since nickel has a pleasing color and takes a high polish, nickel plating is especially desirable for an ornamental finish.

An electrolytically deposited coating is very uniform in thickness and can be made extremely thin. Hence, the method is much used as a means of coating cheap metal with an expensive one, as in making "plated" forks, spoons, and knives for table use, and in the manufacture of cheap jewelry.

424. Protection by Paints. — When large surfaces of iron are to be covered, paints are usually employed as protective agents. This method is seldom completely successful, and the coating of paint has to be renewed frequently. This is largely because the iron is not entirely free from initial rust when the paint is first applied. This rust induces catalytically further rusting underneath the paint, which consequently flakes off. The usefulness of a paint coating depends on the nature of the *paint base* that is mixed with linseed oil in making the paint, and also on minor impurities which are present. Red lead, Pb_3O_4, is usually regarded as the best substance for this purpose. Iron oxide, Fe_2O_3, is cheaper and is much used, but it is not so effective. Asphaltum is applied to the iron used for boilers and sometimes for machinery. Powdered aluminum and, less often, powdered copper are used where a metallic finish is desired.

425. Cement as a Protective Coating. — In recent years, it has been a common practice to cover the steel framework of large buildings with a coating of cement to prevent corrosion. It acts practically as a paint. The thickness of the layer used varies from a brush coating to one of from one to three inches in depth. Experiments have indicated that this gives a method of greatly retarding the rusting. But we cannot be certain that it gives a *permanent* protection, for the reason that not enough time has passed to enable us to judge. Cement is superior to paint in that it does not easily flake off. Furthermore, since cement is alkaline, it tends to prevent rusting, as we have seen that iron does not corrode readily in the presence of alkalies. But cement is porous, and water and the gases of the air will diffuse through it. Hence it is quite possible that rusting may occur slowly underneath the cement.

426. The Magnetic Oxide of Iron as a Protective Coating. — The magnetic oxide of iron, Fe_3O_4, makes a very effective protective coating for iron if it is deposited on the surface of the metal in a firmly adhering layer. This oxide is very different from ferric oxide, Fe_2O_3, since it has no catalytic effect in inducing oxidation. The process consists in subjecting the hot iron or steel to the action of a mixture of superheated steam and carbon dioxide. The carbon dioxide prevents the formation of any ferric oxide. The equation is:

$$\underset{\text{iron}}{3\,Fe} + \underset{\text{water}}{4\,H_2O} \longrightarrow \underset{\substack{\text{magnetic}\\\text{iron oxide}}}{Fe_3O_4} + \underset{\text{hydrogen}}{4\,H_2}$$

This affords what is probably the best protective coating for iron and steel. Spots of rust do not readily spread if they form where the coating has by chance worn off. The process has the disadvantage that it cannot be applied to metal that has been put in place in structural work. Each piece must be separately treated at the factory, and it cannot be hammered or riveted into place, as this treatment would break the coating, and give rise to local rusting.

Russia iron is iron covered with a coating of magnetic oxide. It is used for stove pipes, the covering for locomotive boilers, and similar purposes.

SUMMARY

Various Constituents of the Air act with greater or less rapidity on metals. This action does not seriously affect most metals, except in appearance, because the action stops after a thin layer of corroded matter has been formed.

The Corrosion of Iron, however, is a very serious matter, since the rust, when once formed, acts as a catalytic agent for the formation of more rust. Consequently the metal may rust through in a comparatively short time. *Iron rust* consists of a mixture of ferric oxide, ferric hydroxide, and ferrous carbonate.

Iron does not Rust in the presence of bases, but corrodes very rapidly in the presence of acid fumes. A commonly accepted theory of its corrosion is based on the fact that carbon dioxide and water form a weak acid, carbonic acid. The theory is that the rusting starts with the action of this acid, and that ferrous carbonate, $FeCO_3$, is formed; that this substance is next changed by moisture and oxygen of the air into ferric hydroxide, $Fe(OH)_3$, with the liberation of carbon dioxide. This liberation of carbon dioxide "on the spot" explains why rusting proceeds very rapidly where it has once started. The ferric hydroxide is partly decomposed into ferric oxide, Fe_2O_3, and water.

Iron is protected against Corrosion by these methods: (*a*) painting, which is not very effective, and which must be done repeatedly; (*b*) coating with cement, which is more successful, but not necessarily wholly effective; (*c*) coating with magnetic oxide, Fe_3O_4, by the action of steam at a high temperature; (*d*) dipping the iron into melted tin (tin plate) or melted zinc (galvanized iron); (*e*) electroplating with either zinc, copper, or nickel.

EXERCISES

1. What connection is there between the chemical activity of a metal and the ease of its corrosion? Name two active metals; two moderately active metals; two inactive metals.

2. What constituents of the air cause the corrosion of iron? Of silver? Of copper?

3. Explain why iron tools rust much more rapidly in a chemical laboratory than elsewhere.

4. State a theory that explains the rusting of iron by the constituents of the air.

5. Why do surgeons, in sterilizing their instruments, boil them in a solution that contains a little alkali?

6. Which substance makes the best material for roofing or cornice work: tin plate, galvanized iron, or copper? Why?

7. Why was lead so frequently used as a roofing material for castles and cathedrals during the Middle Ages?

8. What is meant by saying that "iron rust is a catalytic agent for its own formation"?

9. Why are tools, when bought at a hardware store, frequently found to be covered with grease?

10. What is tin plate? How is it made? What is galvanized iron? How is it made?

11. In what ways is a covering of nickel superior to one of tin or zinc?

12. Why are iron kitchen utensils and dishes usually covered with tin in preference to other metals?

13. What precautions should be taken before applying paint to iron structures? Why is it necessary to repaint such structures frequently?

14. What advantages has concrete as a protective coating for iron?

15. Concrete that contains iron or steel reënforcing rods is occasionally found to be burst open from within. How would you explain this?

16. What is Russia iron? How is it made? What are its advantages? What are its disadvantages?

17. The tin covering on tin plate usually has small pin holes. Why is this a serious disadvantage?

CHAPTER XXXIX

CLEANING OF METALS

427. Polishing and Polishing Powders. — As we have seen, metallic objects which are not thoroughly covered with protective coatings become corroded or tarnished by the action of various constituents of air and water. Even without a protective coating, this tarnishing is largely prevented if the articles are in constant use so that the tarnish is worn off as fast as it forms. For example, the tools that a workman is using all the time do not rust, while those of only occasional use should be wiped after use with an oily cloth to keep them bright. Coatings of rust or tarnish may be removed by abrasion, that is, polishing with a material harder than the coating. In such a process the fine, gritty particles of the abrasive scratch off the rust, and, if they are hard enough, finally scratch the metal also.

The two essentials of a good polishing powder are :

(*a*) it must be harder than the layer of corroded matter,

(*b*) its particles must be so fine that they will not make noticeable scratches on the surface of the metal.

A very hard abrasive should not be used on a soft metal, as it will remove too much of the metal itself with the corroded layer.

A deposit known as *infusorial earth* (Fig. 141) is found in many localities. This mainly consists of glassy skeletons of microscopic plants, and is chiefly silicon dioxide, SiO_2. It is nearly as hard as sand or ground quartz, which is also silicon dioxide. This infusorial earth makes a most desirable polishing powder for metals, as it combines hardness, which makes its action rapid, with exceeding fineness of grain, which keeps it from scratching. It is a very common ingredient of polishing powders, pastes, and soaps. Diatomaceous earth, tripoli, and electro-silicon are other names of this material.

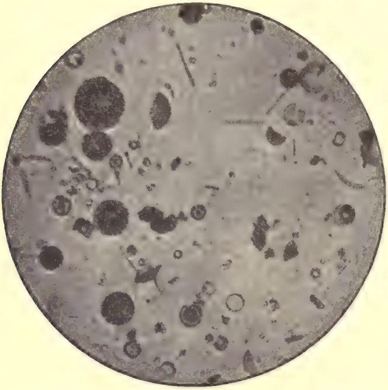


FIG. 141. — INFUSORIAL EARTH, HIGHLY MAGNIFIED.

Powdered silica has largely replaced infusorial earth for all purposes except the finest polishing, because it is much cheaper and purer. It is made by crushing quartz, sandstone, or other silica rock to a fine powder with stamp mills, and grading the powder according to fineness for the different uses to which it is to be put. It is the polishing material contained in scouring soaps and most polishing powders. As powdered silica is always coarser grained than infusorial earth, soaps and powders containing it should not be used on finely burnished surfaces, such as gold and silver. Ground sandstone is often made into scouring bricks, known as Bath or Bristol Bricks.

Another polishing material of similar chemical nature is *pumice*. This is a mixture of silicates ejected from volcanoes as lava. Pumice, even ground to a fine powder, is coarser grained than powdered silica, and so it is more likely to scratch the surface. For coarse polishing, powdered pumice and water are used, then the rough surface is further smoothed with fine pumice and oil.

Finally, infusorial earth is used, as its scratches are too small to mar the surface. Great care must be taken in the final polishing of any article to avoid the presence of a single coarse grain, as that would leave a visible scratch each time it was rubbed over the surface.

428. Ferric Oxide, Fe_2O_3, is extensively used for fine polishing under the names of rouge, colcothar, crocus, and jeweler's red. Both naturally occurring and artificially prepared ferric oxide are used. In either case the material must be ground very fine, carefully washed, and freed from coarse or gritty grains. Rouge is used dry or mixed with water, alcohol, or grease, according to the nature of the work. The red polishing pastes or "Putz pomades" so commonly used consist chiefly of rouge and grease. They are excellent for cleaning all metals except silver and gold. Jewelers use fine-grained rouge for the latter metals, but for household use fine infusorial earth preparations, like electro-silicon, are to be preferred for the precious metals.

Castings and forgings, particularly of iron, usually require a preliminary *grinding* before they are polished. There are three materials widely used for grinding. Silica, SiO_2, is used in the form of sand in the sand blast for cleaning castings, and in the massive form is the chief material in grindstones and oilstones. The second material is aluminum oxide, Al_2O_3. This occurs naturally in the mineral corundum, of which *emery* is an impure form; when prepared in the electric furnace, it is known as *alundum*. Both forms are harder than silica and are widely employed in powder of various grades of fineness and in wheels. Emery powder is also cemented to cloth, paper, and sticks by means of shellac and glue. The third and hardest abrasive is *carborundum*. This is silicon carbide, SiC, produced from coke and sand in an electric furnace (§ 398):

$$\underset{\substack{\text{silicon}\\\text{dioxide}}}{SiO_2} + \underset{\text{carbon}}{3C} \longrightarrow \underset{\text{carborundum}}{SiC} + \underset{\substack{\text{carbon}\\\text{monoxide}}}{2CO}$$

The hard crystals produced in the furnace are crushed and then made up in the same great variety of forms as emery.

429. The Chemical Cleaning of Metals. — This is known as "pickling," and consists in dissolving oxides or other foreign matter by solutions which act on the tarnish. *Iron* is usually pickled in a solution containing one part of sulphuric or hydrochloric acid to ten of water. After the surface is properly brightened, it is thoroughly washed to remove all traces of acid. *Brass* is given a preparatory pickling in sulphuric acid, and then given a second treatment in dilute nitric acid or a mixture of nitric and sulphuric acids. By a proper selection of acids and an adjustment of the strength of the solution, different shades of color may be produced. The solutions described above should be employed in the shop and should not be used in household cleaning, as they are corrosive to flesh and clothing.

Oxalic acid is often used alone or mixed with some of the finer abrasives for cleaning brass or copper ornaments. It is highly poisonous, and articles on which it has been used should be thoroughly washed and dried afterwards. It is not so corrosive as the acids used for pickling, but on account of its poisonous character, it should not be used on anything intended to hold food.

Another poisonous compound used in cleaning solutions by jewelers for gold and silver is potassium cyanide, KCN. This is one of the most deadly poisons known and should *never* be used in the household for any purpose whatever;

a single small crystal is sufficient to cause death. It is deplorable that many cleaning solutions on the market contain this compound. When it is necessary to use a cyanide solution in the arts, rubber gloves should be worn and the hands washed repeatedly after taking them off. Enough might enter the system through a scratch to produce dangerous poisoning or even death. Its value for cleaning metals depends upon the fact that gold and silver, as well as their sulphides, react with it to produce soluble double cyanides. A short immersion removes the tarnish, together with the extreme outer layer of the metal, leaving a bright, clean surface.

430. Household Cleaning. — Some methods of cleaning brass and silver have been given in preceding sections. Another cheap and efficient cleaner for these metals is whiting (finely powdered chalk, $CaCO_3$) moistened with ammonia. There is no very satisfactory polishing material for nickel which has once become tarnished. Nickel-plated articles, therefore, should be kept free from dirt by washing with soapsuds, and corrosive liquids should be kept from them.

Recently a simple and very satisfactory method of cleaning silverware by boiling it with water in an aluminum dish has been devised. In this case, aluminum replaces the silver in the compounds forming the tarnish. In cleaning plated silver, the fact that the plating is pure silver and hence softer than ordinary sterling or coin silver should be kept in mind. Plated silver should never be rubbed hard, even with abrasive polishes which might be suitable for solid silver. If the plated ware is lacquered in addition, then only water and a soft cloth should be used. If the lacquer is once pierced, the exposed silver will begin to tarnish. The lacquer should then be entirely removed and the piece may either be relacquered or be treated like other plated silver.

Slight discolorations in aluminum kitchen ware may often be removed by cooking some acid fruit or vegetable in the dish. Aluminum may be readily cleaned by scouring with Dutch Cleanser, Bon Ami, Sapolio, or any other cleansing powder or soap containing little free alkali. Soda should never be allowed to come in contact with aluminum, for it will turn the aluminum black. This black coating or any other persistent discoloration may be removed from aluminum by scouring with steel wool (No. 00), moistened with soapsuds.

SUMMARY

Corroded Metal may be cleaned either (*a*) by rubbing off the coating with an abrasive, or (*b*) by chemically dissolving it. Abrasives must be a little harder than the coating to be removed and so fine-grained as not to scratch the metal perceptibly.

Finely divided Silica (infusorial earth or ground quartz) is an excellent polishing powder. Ground pumice stone is used with water for coarse polishing, and with oil for fine polishing.

Rouge, ferric oxide, is used either dry or wet with water, alcohol, or grease for cleaning all metals except gold and silver.

Castings are smoothed with sand, sandstone, aluminum oxide or carborundum.

Iron is pickled in dilute sulphuric or hydrochloric acid.

Brass is pickled first in dilute sulphuric acid and then in dilute nitric acid.

Oxalic Acid is valuable for cleaning brass and copper. It is poisonous.

Potassium Cyanide is used by jewelers to clean gold and silver. It is exceedingly poisonous.

Silverware may be cleaned by boiling in pure water in an aluminum dish. Plated silver should never be scoured or rubbed hard.

Aluminum may be cleaned with a non-caustic cleaner. Bad discolorations may be removed by scouring with soap and steel wool.

Whiting, moistened with ammonia, is a cheap and efficient polishing material for brass, copper, and silver.

EXERCISES

1. What is the composition of the surface coating to be removed from tarnished silver? Copper? Zinc? Rusty iron?

2. Why do the blades of pocketknives rarely require polishing?

3. Why is sand suitable for grinding, but not for polishing?

4. Give in detail the steps necessary to convert the casting for a brass ink stand into the finished article.

5. Will a scouring soap completely dissolve in water? Explain.

6. Give the composition and use of each of the following: tripoli, emery, carborundum, Putz-Pomade, electro-silicon.

7. Describe a method of cleaning silver spoons (*a*) for household use, (*b*) for jeweler's use. Why should the jeweler's cleaner not be used in the house?

8. What is "pickling"? Give the proper pickle for iron; brass; gold.

9. Why may carborundum powders of different degrees of fineness be used in finishing the same article?

10. Give two methods of cleaning a brass door knob.

11. Why is it well to avoid silver polishes advertised to "clean without labor"?

12. Give two methods of cleaning an aluminum dish and state when each should be employed.

CHAPTER XL

IRON AND STEEL

431. Classification of Iron and Steel. — Iron is not produced commercially in a pure form, as copper is, but always contains a certain proportion of carbon and other substances. Differences in the proportion of carbon particularly, and in the way in which the carbon is physically and chemically related to the iron, give rise to a large number of metallic substances which may be included under the general classes, *cast iron*, *wrought iron*, and *steel.* The differences in the properties of the finished products are due to the character of the original ore, to substances added to or taken from the ore, and to the heat treatment received during manufacture. The nature and composition of each of the main varieties of iron and steel will be first examined, and then their properties will be compared.

432. Cast Iron. — Cast iron, or pig iron, is the product formed in the blast furnace by the direct reduction of iron ore with carbon. The ores employed are chiefly oxides, or carbonates which can readily be converted into oxides.

Carbon, in the form of coke or charcoal, is used to reduce the ferric oxide, that is, to separate the oxygen from the iron. A material, called a *flux*, which aids in the reduction of the ore by uniting with the earthy materials in the ore, is also added. For the sake of simplicity, let us consider the impurity in the ore to be silicon dioxide.

This is an acidic oxide or, in other words, the anhydride of an acid, silicic acid

$$\underset{\text{silicon dioxide}}{SiO_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{silicic acid}}{H_2SiO_3}$$

When silicon dioxide is heated to a high temperature with limestone, the heat decomposes the limestone:

$$\underset{\text{calcium carbonate}}{CaCO_3} \longrightarrow \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{calcium oxide}}{CaO}$$

The calcium oxide, which is a basic oxide, combines with the acidic oxide to form a salt, calcium silicate:

$$\underset{\text{silicon dioxide}}{SiO_2} + \underset{\text{calcium oxide}}{CaO} \longrightarrow \underset{\text{calcium silicate}}{CaSiO_3}$$

The calcium silicate, being lighter than the molten iron, separates and forms a layer above it, called *slag*. Other acidic oxides, such as the oxides of phosphorus and sulphur, would combine with the basic oxide, and to a considerable extent be eliminated in the slag.

Sometimes the rock material in the ore is limestone or some other basic rock; in that case silica instead of

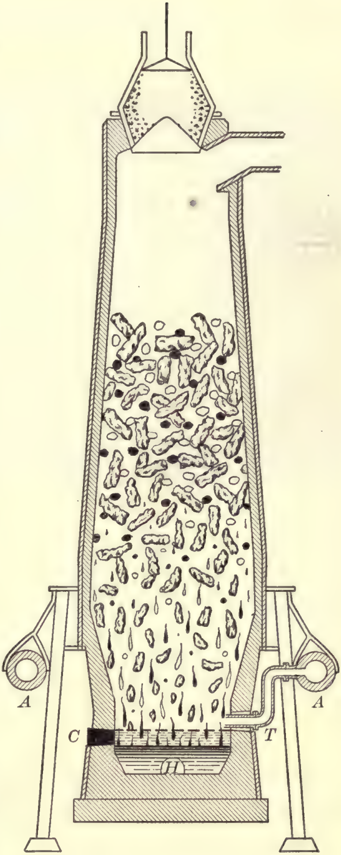
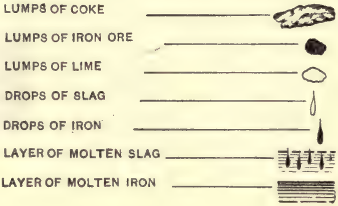
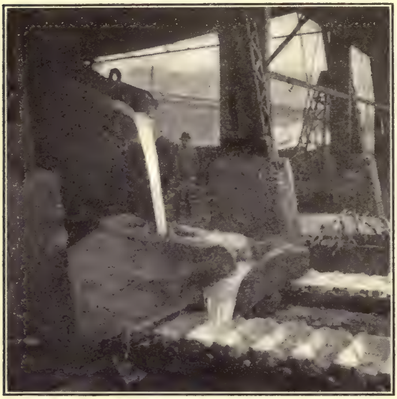


FIG. 142. — BLAST FURNACE. (Sectional.)



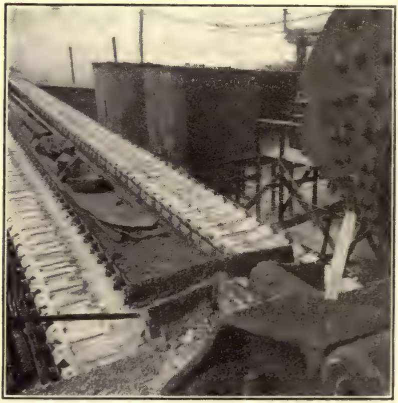
limestone is mixed with the ore to produce the slag. The slag, in addition to gathering the earthy material into a fusible mass, forms a temporary coating on the drops of iron as they work their way down through the furnace, and so protects them from oxidation.



Copyright by the *Keystone View Co.*

FIG. 143. — LADLE POURING MOLTEN CAST IRON.

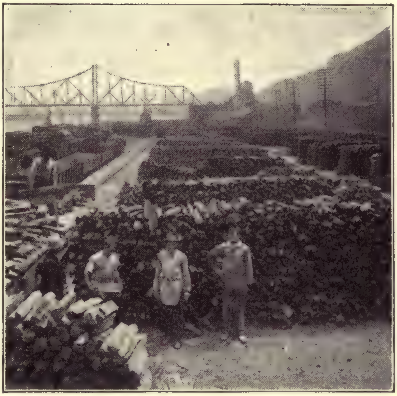
A sectional drawing of the form of furnace commonly used in this country for making cast iron is shown in Fig. 142. Hot, dry air from the pipe "A" is forced through nozzles "T" into the lower part of the furnace. It is this blast of air which gives the furnace its distinguishing name of *blast furnace.* The gaseous products of combustion pass from the furnace through a pipe near the top. The blast air, combining with the coke, raises the temperature of the furnace to the high degree at which ferric oxide is reduced by carbon, and the impurities in the ore enter the slag.



Copyright by the *Keystone View Co.*

FIG. 144. — CHAIN OF MOLDS.

When enough iron has accumulated in the lower part of the furnace, the slag floating on the iron is run off through the slag hole "C," just above the level of the molten iron. The iron is then allowed to run out through the tap hole "H" into a ladle which carries the fluid iron to the casting machine. This consists of molds of iron mounted on an endless chain. A stream of iron is poured into these molds and there solidifies into bars, flat on top and oval beneath, called *pigs* (Fig. 145). From this name the iron is usually called *pig iron* when it is made. The pouring is shown in Fig. 143 and the chain of molds is shown in Fig. 144. When pig iron has been remelted in the iron foundry (§ 440) and formed into useful articles by casting in molds, it is called *cast iron*.



Copyright by the *Keystone View Co.*

FIG. 145. — PIG IRON IN A METAL YARD.

Cast iron is the most impure form of iron, containing from 2% to 7.5% of carbon, in addition to other impurities, the most important of which are sulphur, phosphorus, and silicon. Commercial grades of cast iron contain from 3% to 4.5% of carbon. The carbon is partly combined with the iron in iron carbide, Fe_3C, and partly scattered through the metal in flakes of graphite.

433. Nature of Steel. — Steel differs from cast iron in composition in two particulars: 1st, it contains less than 2% carbon; 2d, none of the carbon in steel is in the form of graphite, but is combined with the iron in iron carbide, Fe_3C, which is in solid solution in the metal. The percentage of carbon in steel and the heat treatment which the steel has received in its production from cast iron, together determine the properties of the steel produced. When the percentage of carbon is below 0.3 %, the steel is known as *low-carbon*, *soft*, or *mild* steel. With 0.3 % to 0.8 % of carbon, the steel is *medium-carbon* or *half-hard* steel. From 0.8 % to 2.0 % carbon produces *high-carbon*, *hard*, or *tool* steel. These limits are approximate, particularly with reference to the hardness, as this property is largely modified by the heat treatment. The manufacture and properties of the various kinds of steel will be discussed later in the chapter.

434. Nature of Wrought Iron. — In the percentage of carbon, wrought iron has the same limits as low-carbon steel, from 0.05 % to 0.3 %. The essential difference between wrought iron and mild steel is the fact that the manufacture of wrought iron leaves a small percentage (0.2 % to 2.0 %) of slag in the finished iron. The method of working wrought iron causes the slag to take the form of long rods extending through the mass of the iron, and so gives wrought iron a fibrous structure not found in steel. The latter is completely melted during its formation, and the slag rises to the top and is removed; steel, on solidifying, has a crystalline structure throughout.

435. Bessemer Process. — This process consists essentially of removing from pig iron nearly all of the impurities by oxidation, and then adding enough carbon to give the percentage desired in the steel. The molten iron from the blast furnace is run into a ladle, instead of into molds, and is poured into a huge pitcher-shaped vessel, called a *converter*. A blast of air is driven up through the metal in the converter from the bottom, in order to oxidize the impurities. The acidic and basic impurities unite, while the carbon is converted into carbon dioxide. The details of the converter are shown in Fig. 146. The heat liberated in the process keeps the metal fluid, and the action continues until the iron begins to oxidize, a point which is indicated by a change in the color of the flame. At this instant a special iron, rich in carbon, manganese, and silicon, is added to the charge in the converter in the proportion necessary to give the steel the desired composition. The manganese prevents the formation of iron oxide; and the silicon, the formation of bubbles of gas, or blowholes. The action is continued just long enough to incorporate thoroughly the alloy with the metal. Then the converter is tipped on its axle and the steel run into a ladle, from which it is poured into a series of ingot molds, standing on a train of cars near the converter.

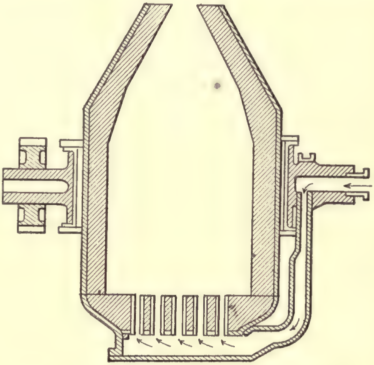


FIG. 146. — BESSEMER CONVERTER.

The composition of the converter lining affects the character of the steel produced and determines the kind of pig iron that may be made into steel by this process. When the lining is "acid," that is, composed chiefly of silica, only pig iron containing a small proportion of phosphorus can be employed, as the phosphorus is not burned out under these conditions. With a "basic lining," the essential constituents of which are calcium and magnesium oxides, the phosphorus is more completely eliminated, lower-grade pig iron can be used, and a better quality of steel produced.

Since the entire Bessemer process occupies less than half an hour and as much as 20 tons may be handled in a single converter, it will be readily seen that the product will be less uniform than that produced by a slower process. Bessemer steel is used generally for rails and often for the less important kinds of structural work. Where a greater degree of uniformity and reliability is required, steel made by the slower open-hearth process is generally preferred.

436. Open-hearth Process.— In this process the impurities in pig iron are oxidized by the addition of iron oxide and diluted by the addition of scrap steel. The charge, consisting of pieces of pig iron, iron ore, and steel scrap, is melted by the flame of a mixed blast of air and gas, pass-

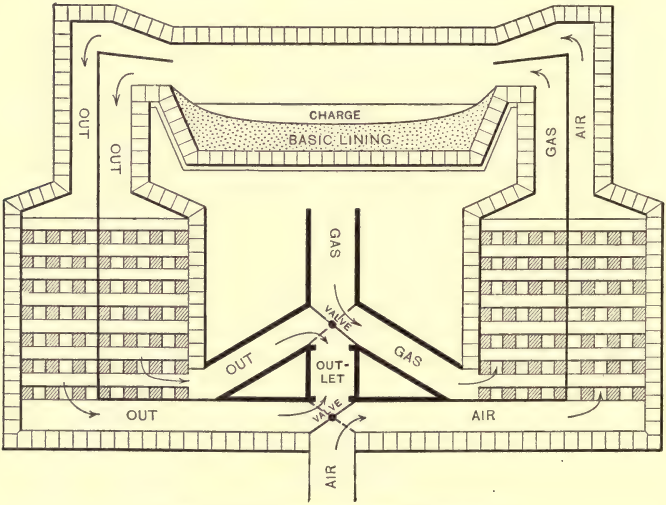


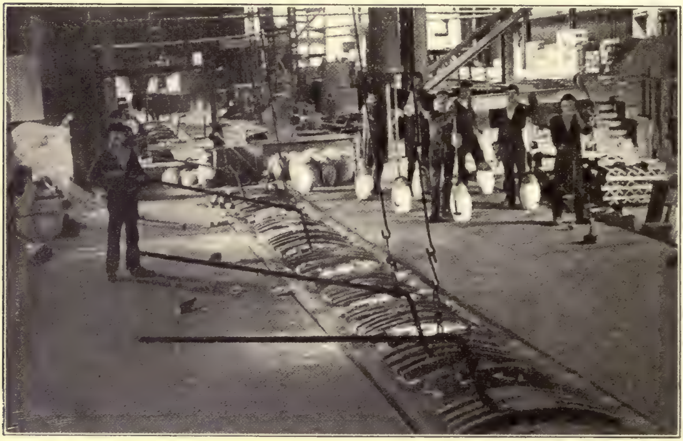
FIG. 147. — OPEN-HEARTH FURNACE.

ing over the hearth of a saucer-shaped furnace (Fig. 147). This furnace may have either an acid or a basic lining, as in the case of the Bessemer coverter, with the same differences in the character of the pig iron employed and in the composition of the steel produced. When a basic lining is employed, the slag produced contains phosphates, which are valuable as fertilizer. As this process takes as many hours as the Bessemer process does minutes, samples of the product can be withdrawn at intervals and their composition determined. Thus the character of the product may be much better controlled than in the coverter.

In the open-hearth furnace, there is a pair of brickwork chambers, through which the air and gas pass before mixing at the mouth of the furnace, and a similar set through which the products of combustion pass on their way to the chimney, heating the bricks very hot in their passage. By reversing the direction of the gases at intervals, the incoming air and gas are heated exceedingly hot before they meet and burn in the furnace. In this way a very intense heat is produced in the furnace chamber with an economical use of fuel.

Open-hearth steel is used for bridges, armor plate and the better class of structural work, and also for conversion into the high-grade tool steel.

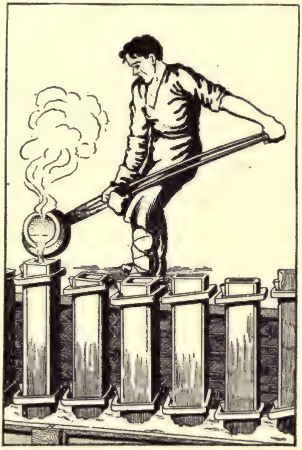
437. High-grade Steel. — For uses demanding the greatest uniformity and freedom from undesirable impurities, further refining than is obtained in the processes just described is necessary. Of a number of processes which are in use, the most important are the crucible process and the electric furnace process. In the *crucible* process, wrought iron or steel is remelted in a graphite crucible, usually having a capacity of about 100 pounds (Fig. 148). When wrought iron is used, the proper percentage of carbon is secured by the addition of charcoal to the iron before melting. As very pure wrought iron can be obtained, a high degree of purity can be secured in the steel. When steel is used as the crucible charge, it has usually been made by heating wrought iron bars for a long time in contact with carbon; this results in iron carbide forming and entering into solid solution with the iron, chiefly near the surface. The main object in remelting in the crucible in this case is to secure greater uniformity in the product. The crucible process is now chiefly used to manufacture various alloy steels, in which nickel, tungsten, or other metals are introduced to secure special properties.



Courtesy of the *Crucible Steel Co. of America.*

FIG. 148. — CRUCIBLE MELTING FURNACES.

The crucible process is expensive when considerable quantities of high-grade steel are to be made, and is being replaced by the *electric furnace* process. By this process Bessemer steel can be quickly and cheaply converted into steel as good as the open-hearth product, or open-hearth steel can be converted into high-grade steel in less time and at less expense than by the crucible process. The furnace proper is similar to the open-hearth furnace, and is so arranged that it can be tipped for pouring the metal at the end of the operation (Fig. 128). Instead of the elaborate arrangement for heating by gas, there are, in the simplest form, two graphite electrodes which can be lowered into the slag floating on the metal, which is molten when placed in the furnace (§ 403). The resistance offered to the current develops an intense heat, and sulphur and phosphorus are oxidized by iron oxide and lime that is thrown in ; a slag is formed on top as a result of the action of these materials with the impurities in the metal. The carbon is almost entirely burned out and the proper amount is introduced by the use of recarbonizing alloys, as in the Bessemer and open-hearth processes. By a proper choice of the material added, a high-grade carbon steel or alloy steel of any desired composition can be produced. Amounts as high as 15 tons can be made at one operation, which is completed in 2 hours. The excellent quality of the steel, the great range of different steels that may be produced in the same furnace, and the large reduction in the amount of manual labor required, make it probable that the electric process will almost entirely replace the crucible process, especially for the manufacture of large quantities of steel.



Courtesy of the *Crucible Steel Co.*

FIG. 149. — POURING STEEL INGOTS.

438. Manufacture of Wrought Iron.— The raw material of wrought iron, like that of steel, is pig iron and the process is essentially a purifying process. The difference between this and the steel process is that in making wrought iron the metal is never completely melted. The furnace used is a reverberatory furnace. The fire is in a compartment at one end and the flames pass over the hearth of the furnace, which lies beyond. The arched roof over the hearth reflects the heat down upon the charge, as the products of combustion pass to the chimney beyond (Fig. 119). The charge on the hearth consists of pig iron and iron ore (iron oxide). Under the influence of the heat, the oxygen from the ore oxidizes the impurities in the pig iron and the ore is itself reduced. The impurities unite in a slag. By constant stirring with iron rods through openings in the side of the furnace, the entire charge is exposed to the heat and the impurities in the pig iron finally reduced to a very small amount. Impurities always lower the melting point of a solid. Pure iron has a higher melting point than impure iron. As the iron increases in purity, it separates from the impure mass.

Since the metal is only heated hot enough to reach a pasty condition and not to melt completely, the slag does not rise in a distinct layer to the top, but permeates the entire mass. Near the end of the process the workmen gather the pasty mass into balls. This process is called "puddling." The balls of iron are removed from the furnace and, while still hot, most of the slag is squeezed out by hydraulic presses or by great steam hammers. As has been stated, the slag is not completely eliminated, and the resulting network of slag in the iron after it has been hammered and rolled, gives wrought iron its characteristic fibrous structure. Aside from the presence of the slag, the percentage composition of wrought iron is essentially that of low-carbon steel. There is, however, a considerable difference in the properties of the two, resulting from the difference in physical structure.

439. Effect of Impurities on the Melting Point. — As in the alloys, the melting point of iron is lowered by the addition of another metal, or of a soluble impurity, such as carbon or iron carbide. So we find that the purest irons and steels, such as wrought iron and low-carbon steel, have the highest melting points. As the percentage of carbon increases, the melting point drops, therefore the high-carbon steels have lower melting points than the low-carbon steels, while cast iron is lower still. Pure iron has a melting point of about 1500° C., while 1400° C. may be taken as a representative melting point for high-carbon steel and 1200° C. for cast iron. The lowest melting point obtained (1050° C.) is for cast iron with 4.3% carbon, and for higher percentages of carbon the melting point rises again. This minimum melting point corresponds to the cast iron having the most uniform structure. The commercial grades of pig iron run from 3 % to 4.5 % carbon.

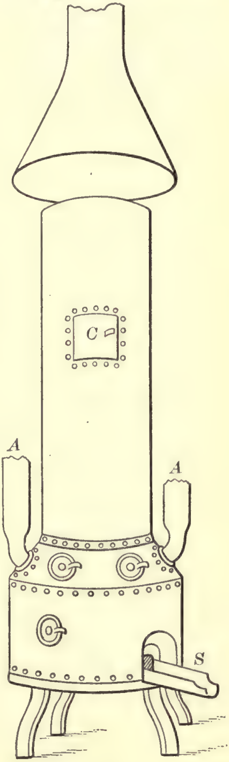
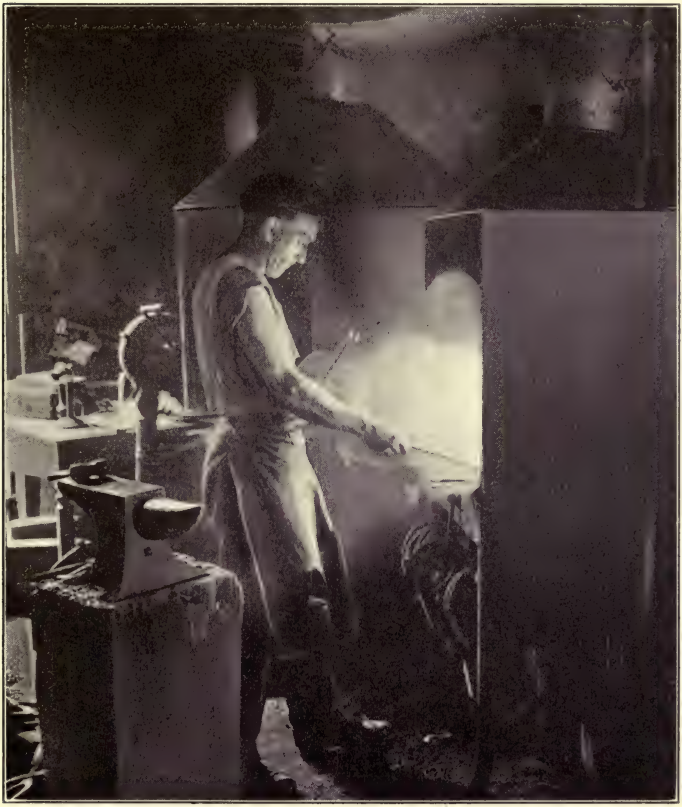


Fig. 150. — Cupola Furnace.

440. Casting of Iron and Steel. — Iron for casting is melted in the *cupola* furnace (Fig. 150). This is essentially similar to the blast furnace in its general structure, although usually much smaller. A mixture of pig iron, coke, and a little limestone is used, and melted by the use of an air blast, as in the blast furnace, although the blast for the cupola is not usually heated. When the iron is in a thoroughly fluid state, it is run off into a ladle. From wooden or metal patterns, sand molds of the objects to be cast have been prepared, and the molten iron is poured into these from the ladle.

The metal for small steel castings may be melted in a crucible furnace, particularly when a special steel is to be used. Bessemer steel may also be cast immediately after pouring from the converter. For most purposes, however, the open-hearth furnace is preferred for the preparation of steel for casting, since the quality of the steel can be more closely regulated than with the converter, and the process is less expensive than the crucible process. Steel castings are often worked under a drop hammer after removal from the mold. They are then called *drop forgings.*

441. Welding. — This is the process of joining, by pressure or hammering, two pieces of metal which have been heated sufficiently to soften them (about 600° C.), but not to melt them. To make a successful weld the surfaces to be joined must be free from oxide, and so some flux (sand or borax), which will form a very fluid slag with the oxide, is commonly used. The hammering expels this slag and allows the chemically clean surfaces to come in contact and cohere. Wrought iron can be very successfully welded and many of its uses depend on this property. Blacksmith's iron is wrought iron. Low-carbon steel, corresponding in composition to wrought iron, may also be welded, but for satisfactory work it must be very pure and very soft. High-carbon steel and cast iron cannot be welded by ordinary means, as they do not soften appreciably until very near the melting point.



Copyright by *Underwood & Underwood.*

FIG. 151.—HEATING IRON FOR WELDING.

In general, the best welds are obtained by using pieces of the same composition. By the use of the electric welder, dissimilar irons and steels may be united. In this apparatus the pieces of metal are held together and a very heavy current of electricity passed through the points in contact. The electrical resistance at the surface of contact causes sufficient heat to raise the ends of the pieces to a welding temperature. In cases of electrical welding of metals which cannot be welded under the hammer, it is probable that the temperature developed is high enough to melt them together rather than to simply weld them. This electric welding is essentially similar to antogenous welding (§ 376).

442. Malleability and Tenacity of Iron and Steel. — Low-carbon iron and steel can be rolled into bars, rails, and plates, and hammered into a great variety of forms, even when cold. As we have seen, when these metals are heated carefully they begin to soften long before they melt. So they are *forged* by heating them red hot and then hammering them into the desired form. This process increases the tenacity of the metal without making it brittle. It is especially true of wrought iron, that the more it is worked, the tougher it is. Bars and plates are made by passing ingots through a succession of pairs of rolls until they attain the desired shape. The drawing of iron and steel wire has already been described (Chapter XVIII, § 172). Hard steel and cast iron are neither malleable nor ductile.

443. Hardness and Tempering. — Differences in hardness in iron and steel depend upon both the carbon content and the heat treatment. Pure iron is comparatively soft and iron carbide is exceedingly hard. In general, therefore, the higher the percentage of iron carbide, the harder the iron. Cast iron is usually very hard; tool steel is used to cut mild steel and wrought iron.

The hardness is affected not only by the amount of carbon present, but by the form in which the carbon exists in the iron or steel. The way in which the carbon is held in the steel depends upon the heat treatment the steel has received. When steel is heated to a high temperature and then suddenly cooled, the iron carbide is chiefly retained in solid solution. This process makes the steel harder, particularly when the proportion of carbon is high. Sudden cooling does not allow time for the change from solid solution to a mixture of iron and iron carbide to take place. The solid solution cannot change into a mixture of iron and iron carbide at ordinary temperatures.

If the steel is now heated to a temperature below that at which it was hardened, the increased temperature permits the change just mentioned to take place, and the steel is softened or *tempered.* The higher the temperature, within certain limits, to which the hardened steel is raised, the softer it becomes, because there is more freedom to change to iron and iron carbide from the harder solid solution. After tempering, the steel may be cooled quickly or slowly with no great difference in the final hardness, for the greatest amount of the softening process possible has already taken place at the high temperature, and as it cools no further change will take place. The degree of tempering is estimated by the color of the oxide that forms on the surface, a straw yellow corresponding to the hardest steel and the familiar blue color of saws corresponding to a comparatively soft steel. A watch spring illustrates the fact that a steel heated to a high temperature is not very brittle, as it can be bent nearly double before it breaks. Files, on the other hand, which are tempered at a low temperature, are very brittle. The following table shows the color of the surface oxide and the corresponding temperature of tempering, together with the use of the steel.

COLOR	TEMPERATURE	STEEL USED FOR
Pale yellow	430°–450°	Razors
Full yellow	470°	Penknives
Brown	490°–510°	Shears and tools for brass work
Purple	520°	Table knives
Blue	530°–570°	Watch springs and sword blades
Blue-black	610°	Saws and other woodworking tools

444. Magnetic Properties. — All varieties of iron and steel show magnetic properties at ordinary temperatures, which disappear when the metal is heated to about 700° C. There is a marked difference, however, between the magnetic behavior of the low-carbon and the high-carbon varieties of iron and steel. The purest and softest grades of wrought iron are magnetized more easily than any other forms of iron, but this magnetism is temporary and, when the iron is removed from the magnetizing field, it has but little permanent magnetism. Low-carbon steel, which has been slowly cooled, behaves in the same way as wrought iron, which it closely resembles in composition. High-carbon steel, particularly when hardened, has very different magnetic properties. Under the same magnetizing force, a piece of high-carbon steel will be a much weaker magnet than a piece of wrought iron. When the magnetizing force is removed, however, the steel will retain a much larger amount of permanent magnetism. Therefore soft (low-carbon) iron and steel are used in making electromagnets, as in motors, dynamos, lifting magnets, etc. These magnets may be very strong when an electric current is passing through a coil of insulated wire wound on the iron core, but lose most of their magnetism as soon as the current is cut off. When a permanent magnet is desired, high-carbon steel, or alloy steel, is made into the desired form, hardened, and then magnetized. Medium-carbon steel and iron show magnetic properties intermediate between those of the low-carbon and high-carbon varieties.

Numerous physical experiments have led to the conclusion that magnetizing a piece of iron consists in turning its molecules into a definite arrangement. It is believed that only molecules of that variety of pure iron which is stable below about 700° C. can be so rotated. The presence of iron carbide and of iron with dissolved carbon seems to interfere with the rotation of the molecules. This would account for difficulty in strongly magnetizing cast iron and high-carbon steel, and also for the retention of magnetic power by these metals. The presence of other metals, such as manganese, in alloy steels often interferes with the ease of magnetizing and demagnetizing. Permanent magnets are "aged" by keeping them in high-temperature steam for a considerable time. Magnets so treated can be relied upon to maintain a constant strength for a long time.

445. Uses of Iron and Steel. — *Wrought iron* is used for wire, sheet iron, ornamental iron work, cores for electromagnets, blacksmith's iron, cut nails, and other uses demanding a malleable, ductile iron, which can be welded and whose magnetism is temporary.

Low-carbon steel is used for boilers, tubes, rivets, bridge work, ships, wire, nails, sheet steel, dynamo frames, and electrical castings.

Medium-carbon steel is employed in making railroad rails, axles, shafting, machine parts, and castings. When tempered and hardened, it is sometimes used for low-grade springs and cheap cutlery.

High-carbon steel is nearly always hardened and tempered. It is used for cutting tools, springs, files, etc. It is the strongest, hardest, most elastic and most expensive form of steel.

Cast iron is used in making pillars, the beds of machines and castings in general. It is also the material which is refined into the other forms of iron and steel. It is hard, brittle, and cheap, with high compressive strength and low tensile strength.

446. Alloy Steels and their Uses. — *Alloy steels* are steels containing other metals, whose presence gives them especially valuable properties. Nickel, manganese, chromium, molybdenum, tungsten, and vanadium are the chief alloy metals used. The alloy steels are all hard, without having the brittle qualities of high-carbon steel. As each has its peculiar excellence, their properties and uses will be considered separately.

Nickel steel contains about 3% to 3.5% nickel and 0.25% carbon. Although this is a low percentage of carbon, the presence of the nickel makes this steel at the same time very hard, very strong, very elastic, and very ductile. It is used particularly for armor plate, bridge cables, and the propeller shafts of steamships.

Manganese steel contains about 12% manganese and about 1.5% carbon. Its most important property is its very great hardness, no matter what heat treatment it has received. When suddenly cooled, it is very ductile; when slowly cooled, it is brittle, so that the rate of cooling has an effect on manganese steel precisely the opposite of that on high-carbon steel. It is used for such purposes as safes, stone crushers, and the cross-overs of railroad tracks. Its use is limited by the fact that it is so hard that tools will not cut it and it must be worked into shape with emery wheels.

Tungsten steel contains from 5% to 10% or even more of tungsten, and from 0.4% to 2% of carbon. It makes very good permanent magnets, as its retentive power is very great. The great hardness of this steel, even at high temperatures, makes it useful in "self-tempering" or "high-speed" metal-cutting tools. A tungsten steel tool will cut without losing its temper, even when the friction developed is great enough to raise the cutting edge to a red heat. This enables it to cut away the metal much more rapidly than a carbon steel tool would do.

Chrome steel, with 2% chromium and from 0.8% to 2% of carbon, is very hard and extremely elastic when suddenly cooled. It is the steel used for the projectiles fired against battle ships. It is employed in rock-crushing machinery and in safes. Chromium is also present in the self-tempering steels.

Vanadium steel combines elasticity with great tensile strength and is much used for automobile frames and parts.

SUMMARY

Iron Ores are chiefly oxides and carbonates. They are reduced by heating with coke in a blast furnace. Limestone or sand is added to the charge to convert the earthy impurities of the ore into slag.

Cast Iron (pig iron) is the product of the blast furnace. Many articles are made from pig iron and steel by melting the metal in a cupola furnace, and pouring the molten metal into molds (casting).

Steel contains less carbon than cast iron, and the carbon is either combined as iron carbide or dissolved in the steel.

The Bessemer Steel Process completely decarbonizes the iron and then the proper proportion of carbon is added.

The Open-hearth Steel Process removes carbon from pig iron by heating with iron oxide until only the desired proportion of carbon remains in the steel.

High-grade Special Steels are produced by the crucible process. Much steel is also made by the use of the electric furnace.

Wrought Iron is made by heating a mixture of pig iron and iron ore in a reverberatory furnace, with constant stirring and working of the pasty mass thus produced. Wrought iron contains very little carbon, but contains some slag. Wrought iron is fibrous and tough.

To weld is to unite by hammering or by pressure two pieces of metal heated sufficiently to soften, but not sufficiently to melt them. Wrought iron and low-carbon steel can be welded.

COMPARATIVE TABLE OF PROPERTIES

	CAST IRON	WROUGHT IRON	STEEL	
			Low-carbon	High-carbon
Carbon, per cent	2% to 7.5%	0.05% to 0.3%	0.05% to 0.8%	0.8% to 2.0%
Melting point, approximate	1200° C.	1500° C.	1500° C.	1400° C.
Structure	Crystalline	Fibrous	Granular or fibrous	Granular
Hardness	Very hard	Soft	Moderately soft	Hard, if tempered
Possible treatment when heated	Can be cast, but not welded nor tempered	Can be welded, but not cast nor tempered	Can be cast and welded, but not tempered	Can be cast and tempered. Not easily welded
Uses	Castings, bases, and columns	Wire, electromagnets and malleable iron	Structural steel, wire, nails, sheet steel	Tools, springs

Specific Properties. — Wrought iron and low-carbon steel are *malleable;* cast iron is not. High-carbon steel can be *tempered* by heating, cooling suddenly, and finally reheating to a temperature depending on the degree of hardness desired. All varieties of iron and steel can be *magnetized;* wrought iron and low-carbon steel most easily; cast iron and high-carbon steel most permanently.

Alloy Steels are noted for hardness, strength, and ability to retain their temper. The most important metals combined with iron in alloy steels are nickel, manganese, tungsten, chromium, and vanadium.

EXERCISES

1. Why is coke mixed with ore in a blast furnace instead of being in a firebox at the bottom?

2. Show how the production of slag is necessary to the reduction of the ore.

3. Why is an air blast used in making pig iron?

4. State the essential differences in composition between steel and the other forms of iron.

5. Show how the proportion of iron carbide affects the properties of steel.

6. Compare Bessemer and open-hearth steel as to (*a*) cost, (*b*) uniformity, (*c*) strength.

7. State the relative advantages of the crucible and the open-hearth processes for making high-grade steel.

8. How does the slag in wrought iron affect its structure?

9. Explain the terms: cupola furnace, ladle, drop forging.

10. What are the advantages of electric welding?

11. Describe the tempering of a table knife.

12. State and explain the difference in magnetic properties between low-carbon and high-carbon steel.

13. Name ten articles of iron or steel found in your home, and state in regard to each whether it is cast iron, wrought iron, high- or low-carbon steel.

14. State the material used for each of the following: stoves, boilers, wire fences, bridges, saws, rails, horseshoes, sheet iron, nails.

15. Give the composition, special properties, and uses of two alloy steels.

CHAPTER XLI

LIME, CEMENT, AND BUILDING MATERIALS

447. Modern Building Construction. — The most notable change in building methods in recent years is the great increase in the use of steel and of concrete in structural work. These materials are at once strong, durable, and non-combustible. It is by their use that huge fireproof buildings can be erected, without the cost being prohibitive. Concrete consists of small pieces of rock material, held together by cement, so the nature and properties of cement must be understood in order to form a proper opinion of what is to be expected of concrete. The other masons' materials, lime, mortar, and stone, may be discussed somewhat more briefly, as they are more familiar.

448. Lime. — One of the most abundant of rocks is limestone, which is impure calcium carbonate, $CaCO_3$. When this is strongly heated, it decomposes; carbon dioxide passes off as a gas and calcium oxide remains as a hard, white solid:

$$\underset{\text{calcium carbonate}}{CaCO_3} \longrightarrow \underset{\text{calcium oxide}}{CaO} + \underset{\text{carbon dioxide}}{CO_2}$$

Calcium oxide is commonly known as *unslaked lime*. The manufacture of lime is carried on in special furnaces, called *lime kilns*. These are usually erected where limestone is found abundantly near the surface of the ground. The older types of lime kilns are often set into the side of a hill, for convenience in charging and removing the lime after burning. The limestone and coal or other fuel are

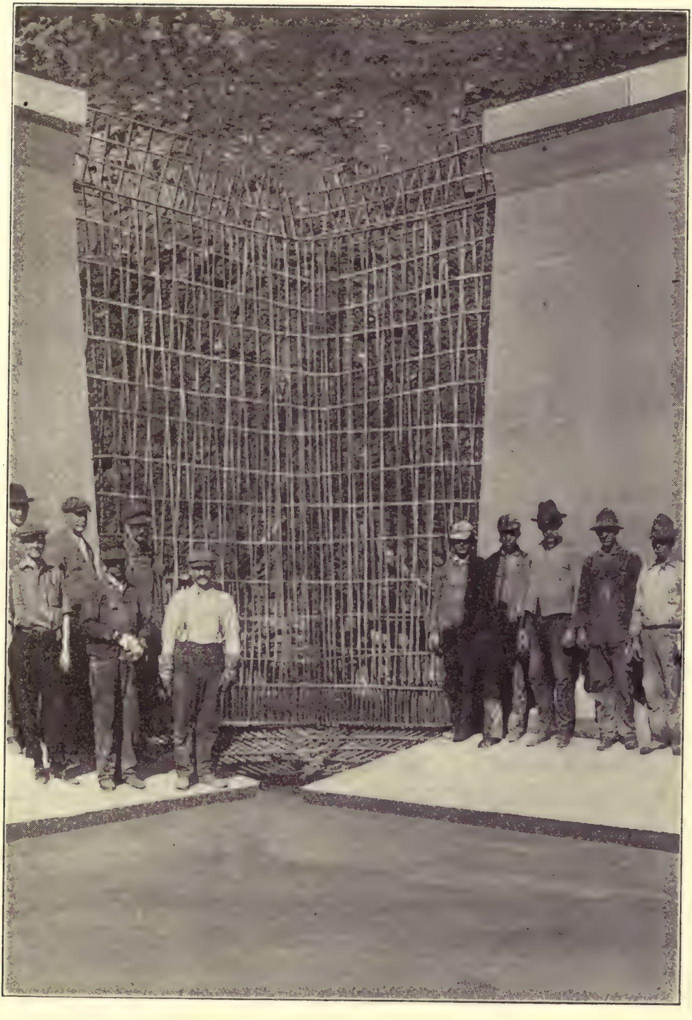


FIG. 152.—REËNFORCED CONCRETE.

mixed and fed into the top. After the fuel has been set on fire, it is kept burning in the lower part of the kiln by withdrawing the burned lime from time to time and adding a fresh charge at the top. In this way the decomposition starts high in the kiln and is completed when the limestone has worked down to where the fire is.

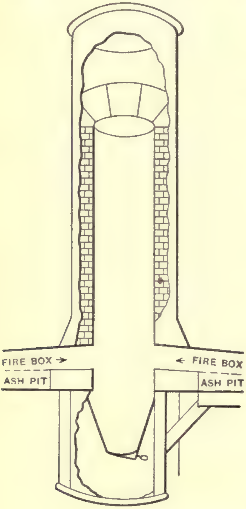


FIG. 153.—LIME KILN.

Lime formed in this way is contaminated with ashes from the fuel. In the more modern kilns, the fires are in side chambers and only the hot gases find their way up through the charge of limestone (Fig. 153). In this way lime free from ashes is obtained.

The best lime is made in a rotary kiln, sometimes as much as 150 feet long and 8 feet in diameter (Fig. 154). The limestone to be burned is first crushed into pieces less than an inch in diameter and is then introduced into the upper, cooler end of the inclined rotary kiln (*K*). This kiln is made of boiler plate, lined with fire brick, and is caused to rotate by a suitable mechanism. Into the lower end is introduced a blast of air and producer gas, or pulverized coal, which burns with an intensely hot flame, extending to a considerable distance in the kiln. The limestone meets the heated gases from the flame as it enters the upper end and it gradually becomes hotter and hotter as it moves down the kiln to meet the flame. During this gradual rise of temperature, the moisture in the stone is first driven off, and then the carbon dioxide begins to pass off. This process is greatly assisted by the constant turning over of the pieces, as they work their way down the cylinder, so that when they reach the intensely hot lower end, where the flame enters, the carbon dioxide has been completely expelled and only calcium oxide remains. The hot lime is dropped from the lower end of the kiln into a rotary cooler (*C*), down which it passes in the same way as it passed through the kiln, and is delivered at the lower end, cool enough for immediate packing or shipment.

The fuel economy of this process is very great. The lime as it moves down the cooler gives up its heat to the air which entered at the lower end. This heated air supplies the blast in the kiln with oxygen, and makes the flame much hotter than if cold air were used. The heated gases from the top of the kiln are carried through a dust settling chamber (*D*) to the boiler (*B*), and there generate all the steam necessary for the producer, the kiln, and the engines used to rotate the kiln and drive other machinery. There are few manufacturing operations in which there is so complete utilization of the heat generated.

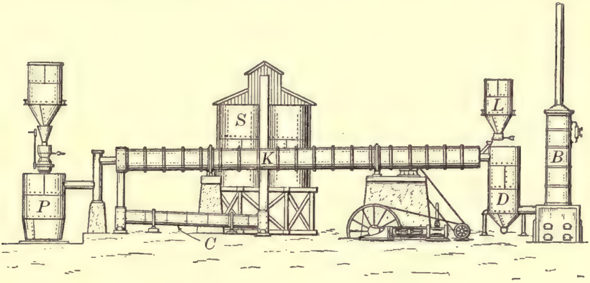


FIG. 154. — ROTARY LIME KILN.

P, gas producer ; *K*, kiln ; *L*, limestone bin ; *D*, dust chamber ; *B*, boiler ; *C*, cooler ; *S*, storage bin for lime.

Lime made in the rotary kiln is superior to that made by other processes, for several reasons. As small pieces of rock are used and all the conditions of burning can be accurately adjusted, the lime is burned throughout, without being overburned, and is free from dust and ashes. It packs more compactly, and for this reason is less liable to air-slake than the larger lumps of varying size produced by the other types of kiln. It is more convenient for the mason to handle, and, on the addition of water, slakes more rapidly and evenly than lime made by other processes.

Water unites with quicklime (calcium oxide) to form *slaked lime* (calcium hydroxide):

$$\underset{\text{calcium oxide}}{CaO} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{calcium hydroxide}}{Ca(OH)_2}$$

A large amount of heat is liberated in this operation, and, before an excess of water is used, steam may be seen rising from lime that is being slaked.

Quicklime exposed to moist air unites with the carbon dioxide present, forming *air-slaked* lime, which is chiefly powdered calcium carbonate, since the calcium hydroxide first formed is converted into the carbonate:

$$\underset{\text{calcium hydroxide}}{Ca(OH)_2} + \underset{\text{carbon dioxide}}{CO_2} \longrightarrow \underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\text{water}}{H_2O}$$

Air slaking makes lime unfit for use in mortar.

449. Mortar. — When sand is thoroughly mixed with wet, freshly slaked lime, ordinary mortar is produced. Mortar is employed to form a hard, stony mass, which holds together the stones or bricks in a building. The hardening of the interior of mortar is chiefly due to the escape of water. The slaked lime forms a kind of jelly-like mass with the water, in which the grains of sand are entangled. As the water evaporates, the calcium hydroxide hardens into a compact, stony mass, and the sand gives additional strength. At the outer surface of the mortar, which is exposed to the air, the hydroxide reacts with the carbon dioxide of the air, forming calcium carbonate. This action takes place slowly, and forms a hard protective outer layer, which prevents water from again entering the mortar and softening the calcium hydroxide. Good mortar strengthens with age, as shown by the solidity of buildings erected centuries ago. Cement is now frequently used in place of part or all of the lime in mortar.

450. Plaster. — The mortar used for plastering formerly had hair mixed with it, to give it greater coherence and make it less liable to scale off when it dried unevenly. The mixture containing cement as well as lime which has recently come into use for plaster, renders the use of hair unnecessary. After the plaster has been mixed, it is spread wet on wooden or metal laths and allowed to become nearly dry. If a smooth finish is desired, the somewhat rough plaster receives an outer coating of powdered lime and plaster of Paris, worked into a paste with water and a little glue or "sizing." This can be finished with a trowel to a smooth surface, which is hard when dry.

Plaster of Paris is made by roasting gypsum, so as to drive off about three fourths of the water of crystallization and leave a fine powder:

$$\underset{\text{gypsum}}{2\,(CaSO_4 \,.\, 2\,H_2O)} \longrightarrow \underset{\text{plaster of Paris}}{(CaSO_4)_2 \,.\, H_2O} + \underset{\text{water}}{3\,H_2O}$$

When plaster of Paris is wet with water and then allowed to dry, it again takes up water of crystallization, forming a hard, continuous mass.

451. Cement. — Hydraulic cement is made by heating a mixture of limestone and clay in a kiln. Chalk or marl may take the place of limestone, since both consist chiefly of calcium carbonate. Shale or slate may be substituted for clay, as all three are chiefly aluminum silicate. The mixture of calcium and aluminum silicates which constitutes cement differs from lime in two important particulars: water does not slake it, but causes it to harden or "set." Therefore cement and sand mixed form a binding material which will harden, even when completely submerged in water.

In a few localities, there exist deposits of "cement rock," consisting of such a mixture of lime and clay materials that cement results from the heating of the natural rock. Such cements are known as "natural" cements, and are usually inferior in quality. *Portland* cement is prepared from an artificial mixture of the limestone and clay rock materials. The composition of Portland cement can be closely controlled, and thus mixtures may be made which will yield the highest grade of cement. *Slag* cement consists of blast-furnace slag mixed with slaked lime.

452. Manufacture of Cement. — Portland cement will be taken as the typical variety, and any points of difference in other varieties will be noted as they occur. The rock materials are carefully and thoroughly ground to a fine powder, first by passing the rock through a series of chilled iron rolls, and later by tumbling in rotating steel cylinders containing steel balls or hard, smooth pebbles. The different rock materials are usually crushed separately at first and thoroughly mixed in carefully proportioned amounts at one of the later stages of the grinding. For Portland cement, the proportion is about 1 part of silica and alumina (clay material) to 3 parts calcium carbonate (limestone, chalk, or marl).

Before "burning," the powdered mixture is dried by heating in rotating drums. The kilns used in burning are inclined steel cylinders, 60 to 150 ft. long, lined with fire brick and kept constantly rotating, like the rotary lime kiln described in § 448. The finely ground cement mixture is fed in at the upper end, and powdered coal, or gas, is forced in under pressure at the lower end. The fuel burns in a long flame, extending a considerable part of the length of the kiln. The rotation of the kiln, together with its inclined position, causes the rock mixture to work gradually down from the upper, comparatively cool, end to the intensely heated lower end. During their passage through the kiln, the materials combine to form a mixture of calcium and aluminum silicates, which is heated before it leaves the kiln to a point where it just begins to melt. Natural cement is not heated in its manufacture to so high a temperature as Portland cement.

The finished material, as it drops out of the bottom of the kiln, is called "cement clinker." This clinker is first cooled and then ground fine by processes similar to those described in connection with the raw material. The finished cement is stored where it will be as little exposed to moisture as possible.

In the manufacture of slag cement there is no burning. The slag, as it flows from the furnace, is granulated by directing a powerful stream of water against it. It is then dried and ground. Dry slaked lime, which is already a fine powder, is added to the partly ground slag and the two materials are ground together to secure intimate mixing.

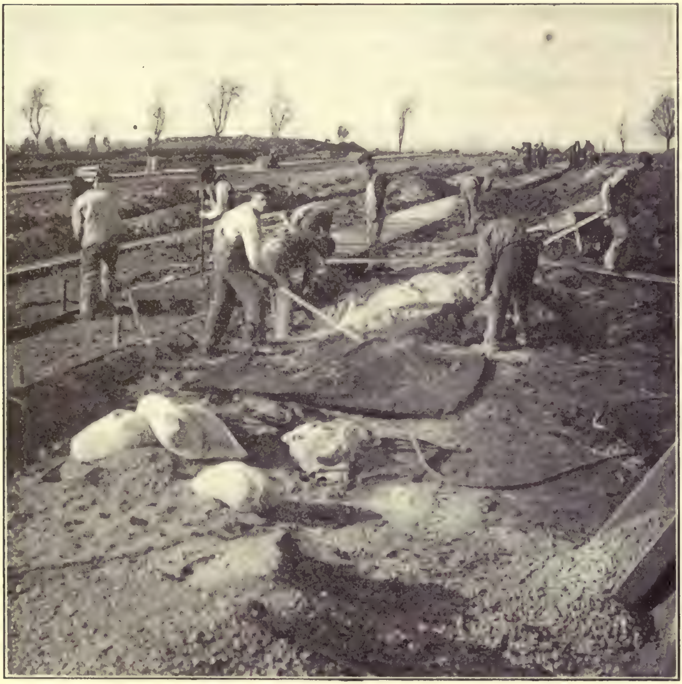
453. Setting of Cement. — When cement is mixed with water and the mass allowed to stand, it solidifies or "sets." The reaction that takes place is probably a conversion of the calcium and aluminum silicates of the dry cement into other silicates of the same metals containing combined water. As the constituents of the air have no part in this reaction, it goes on as well under water as in the air, and as fast in the inside of the mass as on the outside. The increase in hardness and strength goes on rather rapidly during the first few days after the cement is mixed with water, and then more slowly, but the cement continues to gain strength for years. In fact, concrete buildings erected 2000 years ago are still standing and are probably stronger than when they were built.

Calcium hydroxide is probably also set free during the formation of the hydrated silicates and hardens in part by the absorption of carbon dioxide.

454. Concrete. — Cement is seldom used alone, but is mixed with sand, gravel, broken stone, or cinders and water to form *concrete* (Fig. 155). Concrete has not as great strength as pure cement, but pure cement would be far too expensive for use in building construction. The usual proportion in concrete is 1 part of cement to 3 or 4 parts of rock material. This proportion may vary either way in any particular case, as the use of more cement will give greater strength and the use of a larger proportion of stone will make the concrete cheaper.

The strength of concrete is greater when made with gravel than when made with crushed and sifted stone. In either case, the strength is greater if the rock material is nearly uniform in size than if it is not previously graded by sifting. There is a gradual increase in strength in concrete with age, similar to that in cement, which may, however, reach a maximum in about six months and then fall off slightly. A good concrete will sustain a pressure of between 5000 and 7000 pounds per square inch measured when the strength is greatest, without being crushed.

One advantage of concrete as a building material is the convenience with which it may be handled. In building a wall, for instance, the wet concrete is poured into a rough mold made of boards, which may be removed, as soon as the concrete has set, and used over again. Additional strength is secured by setting up in the molds twisted steel rods, running one or both ways. The concrete is then poured in and sets with the rods firmly embedded in it. This kind of construction is known as reënforced concrete (Fig. 152) and is widely employed in the construction of buildings, piers, and bridges. Concrete is sufficiently porous so that it is not entirely water-



Copyright by *Underwood & Underwood.*

Fig. 155. — Making a New Street.

proof, but as long as the reaction is alkaline, the steel rods probably will not rust. We shall not know definitely how much danger of rusting there is until our reënforced concrete structures have stood many years.

Cinder concrete employs the cinders from coal furnaces instead of rock material. The low mechanical strength of the cinders makes this form of concrete suitable only for a fireproofing material in places where it sustains no great weight, for example, for a filling between the floors of a fireproof building. This is the only kind of concrete which can withstand without crumbling the sudden change of temperature resulting from turning a stream of water on a burning building.

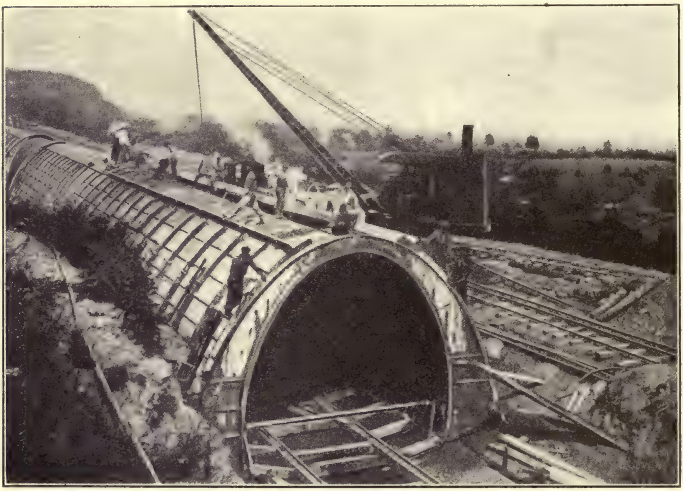


FIG. 156. — CONCRETE WORK ON THE CATSKILL AQUEDUCT, NEW YORK.

455. Building Stone. — There are 3 chief classes of rock material used for building purposes: (1) granites; (2) limestones and marbles; (3) sandstones. The members of each group have similar chemical composition, structure, and origin. The comparative strengths of different building stones is of slight practical importance, as they all have a strength greater than that of the mortar in which they are laid, even if that is a cement mortar. A far more important property is the extent to which a given building stone can resist the action of rain, sun, and frost, that is, its resistance to *weathering.* This property is determined by both its chemical composition and physical structure.

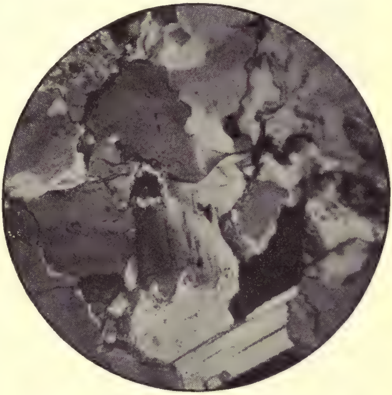
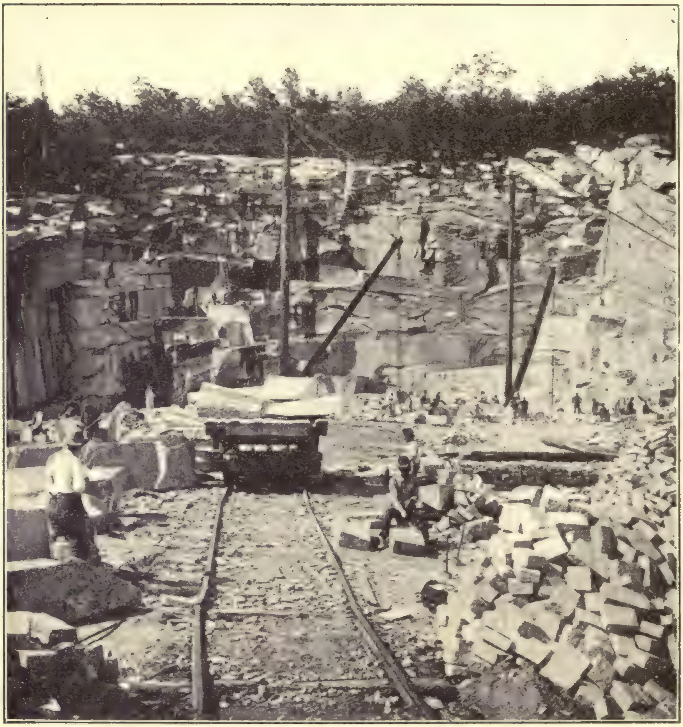


FIG. 157. — HALLOWELL GRANITE. (Highly magnified section.)

Granitic rocks are formed by the action of heat in the crust of the earth, and are very hard. They consist of fragments of quartz, feldspar, and mica welded together into a compact mass (Fig. 157). Quartz is silicon dioxide, SiO_2; feldspar is a silicate of aluminum and one or more alkaline metals, and mica is of similar composition. As granite is very compact, little water enters it, and therefore it is little disintegrated by freezing. None of its constituent materials is very soluble in water, and so the rain does not weather it rapidly. Neither does it break as a result of the variation of temperature between hot days and cold nights. No load that it is called upon to sustain permanently can change its shape. As a result of all these properties, granite may be regarded as the most durable building stone. It is also frequently of great beauty when dressed. On the other hand, the great hardness of granite makes it difficult to dress and it is too expensive for common use.

Limestone consists chiefly of calcium carbonate. It is formed by the gradual deposition of this material under water, or from the disintegration of shells. It is a close-grained, compact rock, of medium hardness. Some limestones, called dolomites, contain magnesium carbonate as well as calcium carbonate. *Marble* is nearly pure, crystalline calcium carbonate (Fig. 159), resulting from the transformation of limestone by the pressure of rocks lying above combined with the heat of the earth. It is valued



Copyright by *Underwood & Underwood.*

FIG. 158. — MARBLE QUARRY. (Concord, N.H.)

as a building stone for the high polish it takes and for its great beauty. Limestone resists weathering better than marble, but neither of them is as durable as granite. As calcium carbonate is somewhat soluble in water containing carbon dioxide, the weathering of limestone and marble is chiefly due to the dissolving of the face of the stone. Neither of these rocks is deformed by any load it is called upon to bear.

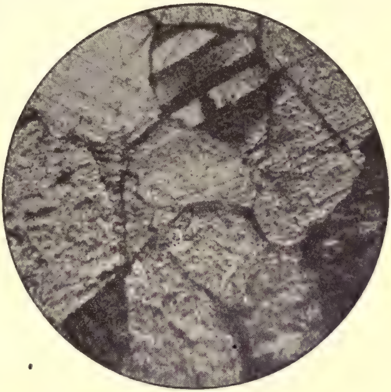


FIG. 159. — MARBLE.
(Highly magnified section.)

Sandstone, as its name implies, consists of grains of sand cemented together more or less strongly (Fig. 160). The cementing materials are silica, calcium carbonate, iron oxide, or clay. When iron oxide is present, the sandstone is red. There are some very durable sandstones, but they are generally too hard to work. The sandstones which are actually employed in building are comparatively porous and soft. They therefore weather badly, breaking up particularly as the result of water getting into the pores and freezing. The cementing materials between the grains are often

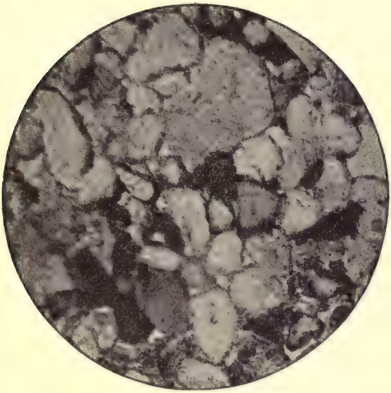


FIG. 160. — SANDSTONE.
(Highly magnified section.)

somewhat soluble also. The elasticity of sandstone is very slight and it takes a permanent set as a result of even light loads.

SUMMARY

Unslaked Lime (quicklime) is made by roasting limestone. It is slaked by mixing it with water.

Mortar is a mixture of slaked lime, water, and sand. The hardening of mortar is due to the escape of water and to the reaction of calcium hydroxide with the carbon dioxide of the air.

Cement is made by roasting a mixture of limestone and clay materials. Cement rock is a natural mixture of these. Portland cement is made from an artificial mixture. Slag cement is blast furnace slag mixed with slaked lime. Cement materials are ground fine, dried, and burned in rotating steel kilns. The resulting clinker is cooled, ground fine, and stored where it will not be exposed to moisture. Cement consists of a mixture of calcium and aluminum silicates. It hardens by the absorption of water.

Concrete is cement mixed with sand, gravel, broken stone, or cinders. It can be conveniently fashioned to any form in molds, and made very strong by embedding steel rods in the mass.

Cinder Concrete consists of cement and coal cinders. Its mechanical strength is very low, but it is valuable as fireproofing.

The Most Important Building Stones are granites, limestones and marbles, and sandstones.

Granite is very hard and consists of quartz, mica, and feldspar. It is the most durable building stone.

Limestone is uncrystallized, and *marble* is crystallized, calcium carbonate. Both are quite durable, but weather slowly by the solvent action of water containing carbon dioxide on the face of the stone.

Sandstone consists of grains of silica cemented together. Building sandstones are soft and porous. They are not durable, their weathering being due to freezing of water in the pores.

EXERCISES

1. Why is limestone more important than any other rock material to the building trades?

2. Distinguish between natural and Portland cement. Which is likely to be the better cement? Why?

3. Describe, with the aid of equations, the manufacture of unslaked and slaked lime.

4. What is air-slaked lime? Why is it not good for making mortar?

5. Why is whitewash (lime and water) a fairly durable inside wall covering, but not satisfactory for outside walls?

6. What is mortar? Explain what takes place when it sets.

7. Why does a mason cover the mortar in his mixing trough with sand, if it is not to be used until the next day?

8. State the difference between mortar and plaster. What is "hard finish"?

9. Why is cement mortar preferable to plain mortar?

10. Why are both the cement materials and the finished cement ground fine?

11. Why do barrels containing lime often burst?

12. What happens in the setting of cement?

13. Compare stone concrete with cinder concrete as to materials and properties. What is reënforced concrete? Give instances of its use that you have seen.

14. Describe the manufacture of a square concrete fence post as you would actually carry it out.

15. Give reasons for the increasingly wide use of concrete.

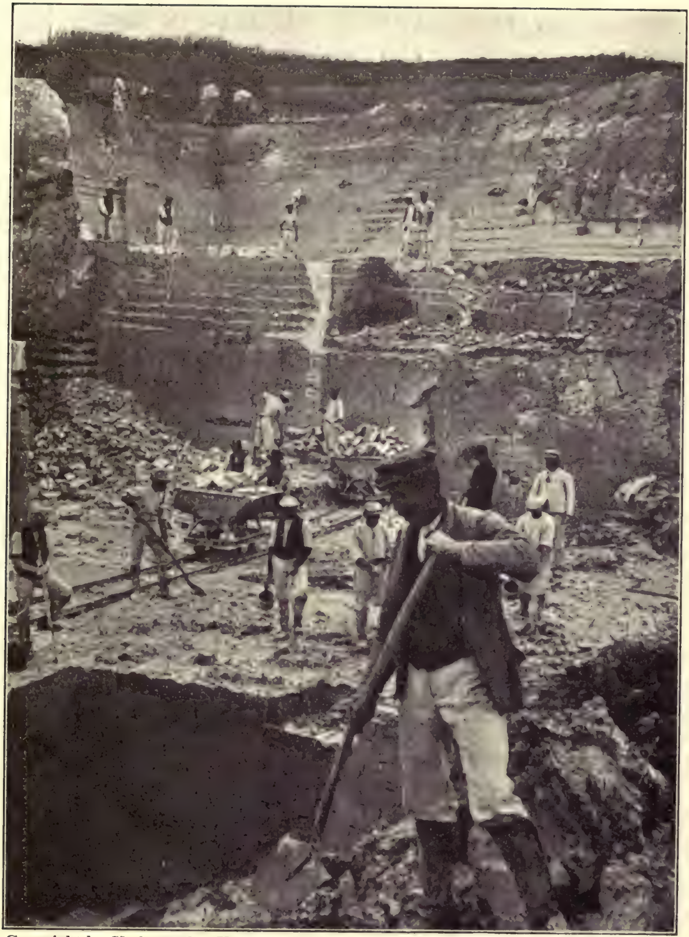
16. Compare limestone and marble as building materials. What are the objections to sandstone as a building material?

CHAPTER XLII

BRICK AND POTTERY

456. Clay. — Clay serves as the raw material for a great variety of industries, and was one of the first natural materials to be employed by man. It is a silicate of aluminum, formed by the decomposition of rocks containing feldspar, which consists of silicates of aluminum and an alkali metal. The properties of clay which make it so valuable are: first, when mixed with water, clay forms a plastic mass, which can be molded readily into any desired form; second, when baked to expel the water, the molded clay becomes hard and possesses considerable mechanical strength, although it is quite brittle. So impure clays are made into brick, drain and roofing tiles, common earthenware and stoneware, while the very pure forms, particularly *kaolin*, are used for the manufacture of fine porcelain and china.

457. Brick. — Ordinary red bricks used for building are made from clay containing some iron compounds, and also, usually, a certain amount of sand or loam. The clay is first pulverized and screened to rid it of coarse particles. The desired amount of water is then kneaded into the clay in a *pug mill*. This is a trough or cylinder with a rotating shaft in the center, in which are set flat paddles arranged in a spiral; as the shaft turns, it thoroughly mixes the clay and water and at the same time forces it along toward the end of the mill. There is a rectangular opening in the end, which corresponds in shape and size



Copyright by *Underwood & Underwood.*

FIG. 161.—GERMAN QUARRY WHERE CLAY IS OBTAINED FOR STEINS AND OTHER POTTERY.

to either the side or the end of a brick. The clay issues from this opening in the shape of a rectangular slab, and is then cut by wires into pieces of the proper size. These pieces are larger than the finished bricks, as considerable shrinkage takes place in drying and burning. The older process of molding the bricks individually by hand is still sometimes followed. After either process, more regular form and greater density may be given the brick by pressing. Pressed bricks are sometimes made directly from the pugged clay without preliminary molding.

After being molded, the moist bricks are set on shelves, or piled on each other, corncob fashion, in sheds, where they are dried either by the heat of the sun or by air artificially heated, until a large part of the water has evaporated. They are then piled in kilns in such a way as to expose as much as possible of each one to the heated gases coming from a series of fires built in the outer part of the kiln. This heating goes on for days, until the greater part of the bricks in the kiln have been properly burned. The red color of ordinary bricks develops during burning, and is the result of the conversion of the ferrous compounds, which give the natural clay a bluish color, into red or brown ferric compounds. Yellow bricks are made from clay containing some magnesium compounds but little or no iron compounds.

The different kinds of bricks owe their colors and other properties to differences in the materials from which they are made, and to differences in manufacture, particularly in burning. *Vitrified paving bricks* are made from clays free from sand. The clay is pulverized much more finely and the temperature of the kiln becomes as high as 800° to 1000° C. Vitrified brick is very close and dense in structure and the individual particles cannot be distinguished, for it is heated in the kiln until it just begins to melt. Vitrified brick is harder than quartz, and makes a very good paving material. The burning and slow cooling of a kiln full of these bricks takes about a month.

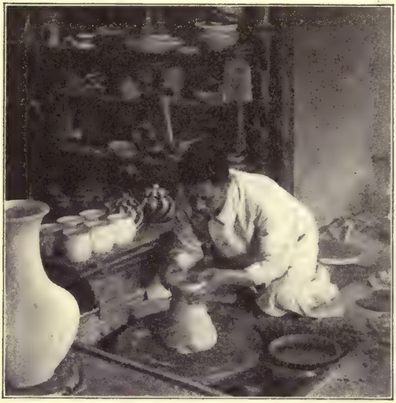
Fire bricks, used for the lining of stoves, furnaces, and fireplaces, are made from clay free from iron and containing a considerable amount of silica. They are burned at a temperature slightly higher than vitrified bricks. When made of suitable material and properly burned, they will withstand the high temperature of stoves and furnaces without either crumbling or softening.

Terra cotta and *hollow tiles* are made of clays similar to those used in building bricks and are burned in much the same way. Flower pots and other articles of unglazed pottery are molded by hand or machine, and then fired. Glazed bricks have a layer of pure white clay over one surface, which is then glazed by the process described below for pottery.

458. Pottery. — Common pottery is made from a grade of clay considerably purer than that used for bricks, but still inferior to the kaolins and other fine clays used for porcelain and china. For white ware the clay must be free from iron, but it frequently contains undecomposed feldspar and other impurities.

The clay is allowed to weather for some time after being dug, and is then thoroughly stirred with water to allow coarse impurities to settle. The thin mud is next strained through fine sieves, and the clay is then put into cloth bags from which the excess of water is squeezed out in a press. It is now ready to be fashioned by the potter.

The chief contrivance used in pottery making is the *potter's wheel*. This consists of two horizontal disks on a vertical axle, so placed that when the potter sits with the upper disk placed at a convenient working height in front of him, he can keep it in rotation by using his feet on the lower disk. Sometimes the wheel is driven by power, with some speed-changing device controlled by the potter's foot. A lump of moist clay is placed on the wheel, which is then set turning, and the potter fashions the clay into any round shape with his moistened fingers (Fig. 162), or with simple metal or wooden tools. After this preliminary fashioning, the wheel is stopped and any modification in shape is made, such as adding a handle or forming a spout. The finished article is removed from the potter's wheel and dried in air for a considerable time, and is then fired.



Copyright by the *Keystone View Co.*

Fig. 162. — Potter at Work.

459. Varieties of Pottery. — All the varieties of clay manufactures described so far are similar, in that, while unglazed, they are *porous* in structure, even after being fired. A glaze not only gives a smooth hard surface, but also fills the pores and so renders the articles water tight. Ordinary tableware has an earthen, porous, opaque body, like earthenware, but it is made of finer and whiter clays and has a finer glaze, which is often transparent. "China" is the name commonly given to the finest grades of ware, which usually have a non-porous body.

Non-porous ware includes hard porcelain, soft porcelain, and stoneware. Some English, French, and Japanese chinas are soft porcelain, but most varieties of fine china are hard porcelain. The difference lies in the kinds of material employed and their relative proportion. Porcelain is always translucent. *Stoneware* is made of inferior materials, and is used for tiles, pipes, parts of chemical manufacturing apparatus, and, with a white, opaque glaze, for "porcelain" bathroom fixtures.

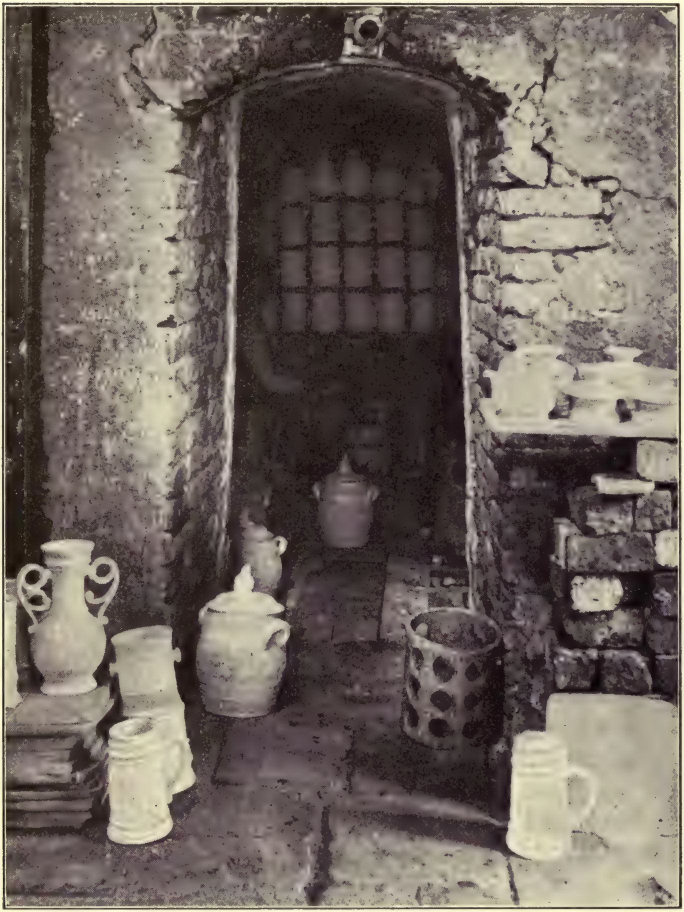
460. Glazes. — The glaze on pottery and porcelain is a hard, smooth outer covering, resembling glass. It must melt at a temperature not exceeding that required to soften the material on which it is placed. The composition of the glaze in any particular case, and the method of applying it, depend upon the article to be glazed and the use to which it is to be put. The glaze on cheap pottery is commonly a mixture of litharge and clay, which melts in the heat of the kiln to form a lead glass, filling the pores and forming a smooth surface coating for the ware. It may be sprinkled on dry, or, as is more commonly the case, applied as a thin mud. Some cheap articles are glazed by vaporizing salt in the kiln during burning. For common earthenware, the construction of the kilns and the piling of the articles inside them is much the same as that described for bricks.

The glazes used in fine wares include a great variety of constituents, each pottery having its own favorite formulas. It is essential that the glaze shall expand and contract at the same rate as the body of the dish. Some glazes consist chiefly of the same material as the body, with just enough other ingredients to secure the essential properties just mentioned. Among these other ingredients are included borax, lead compounds, and sometimes tin compounds. The transparent glazes are usually borax-lead glasses. The beauty of many vases and other ornamental pieces is chiefly due to glazes colored with mineral oxides which will not decompose during firing.

461. Manufacture of Tableware. — The general processes are the same as those described under Pottery. Cups are usually made in plaster of Paris molds, the handles being made separately and attached when cup and handle are still moist. Plates are pressed against a revolving form on a wheel and shaped on the bottom with a tool of the proper shape. The fashioned articles are air dried, then fired, then decorated, glazed, and fired again. In some wares, the decoration is on the glaze instead of under it. The decorative patterns on ordinary tableware are applied to the article with a rubber stamp, or by means of a sheet of tissue paper on which the design has been printed from an engraved plate with mineral colors; the paper is then washed off, leaving the design on the clay. Decoration under the glaze is common in England and on the continent, while the common American practice is to decorate on the glaze. "Hand-painted" china is nearly always decorated on the glaze. All decorated ware is fired for a considerable time after decoration.

The glazes used for tableware are usually harder than those for crockery. For firing, the pieces are placed in fire-clay boxes called "seggers," and the kiln is piled full of the seggers. In firing glazed pieces, each piece must be supported in such a way as not to remove the glaze.

462. Porcelain. — Only the finest and purest clays, feldspar, and other materials can be used for porcelain manufacture. The clays are allowed to "ferment" after being dug, then are ground and washed. The washed clay is kneaded or rolled to make it more uniform, expel air bubbles, and increase the plasticity. The pieces are molded on the wheel, or in plaster of Paris molds, or they are pressed. They are then dried, glazed, and fired. There is only one firing for hard porcelain, at a very high temperature (1300° to 1400° C.), and body and glaze



Copyright by *Underwood & Underwood*.

FIG. 163. — KILN WITH UNBAKED POTTERY.

soften somewhat under the heat and unite to a uniform glass-like mass. Because of the softening, each article must be more completely supported in the segger, and the proportion of distorted pieces is much greater than with ordinary tableware.

English china differs from other porcelains in containing a large proportion of bone ash. It is fired at a lower temperature than the hard porcelains, and so is cheaper to manufacture. The glaze is a boric acid lead glass, having a lower melting point than the body of the ware. *French soft porcelain* (Sèvres) is really a glass ; it softens during burning much more than the hard porcelain and must be more carefully supported. It is glazed with a lead glass, which forms a surface coating only.

Decorative pottery is usually porous in body and owes its value to its beauty of form and to its surface adornment. This may consist of painting under the glaze or upon the first glaze. Some of the richest and most beautiful colorings are obtained by mixing suitable metallic compounds with the glaze before it is applied.

SUMMARY

Clay is a naturally occurring silicate of aluminum, which is plastic when wet, and hard when baked to expel the water.

Bricks are ordinarily molded from clay containing some iron compounds, dried in air, and then baked in kilns. Yellow bricks contain very little iron. Vitrified bricks are made from clay free from sand, and are burned very hard. Fire bricks are made from clay free from iron, but containing considerable silica. Red terra cotta and tiles are made from clay containing iron.

Pottery, earthenware, and china (porcelain) are made from clays purer than those used for bricks. After being fashioned, the articles are air dried, burned, glazed, and again burned.

The Glaze is a hard, smooth, outer coating, resembling glass. It makes the surface smooth and impervious to water.

The Body of bricks, tiles, terra cotta, pottery, crockery, and ordinary tableware is porous. Hard and soft porcelain (china) and stoneware have non-porous bodies.

Decorative Coloring and designs may be under, in, or upon the glaze. The ware is fired after decoration.

EXERCISES

1. Give two important properties of clay.

2. Name four kinds of brick, and give the composition and use of each kind.

3. What is the difference in structure and use between unglazed tile and vitrified tile?

4. Why is it better to grow plants in flower pots than in glass jars?

5. State in order the operations which a piece of freshly dug clay undergoes during its conversion into a decorated dinner plate.

6. Name five articles which might be fashioned on the potter's wheel; two which are otherwise molded.

7. Why must a glaze have a melting point lower than that of the article to which it is to be applied?

8. Why is tableware always glazed?

9. Why is it unsanitary to use cracked dishes?

10. Why should the glaze when heated have the same rate of expansion as the body of the dish?

11. Under what circumstances would a transparent glaze be used?

12. Give at least two reasons why it is more expensive to make an undecorated thin china cup than a cup of the same capacity made of common crockery.

13. Name two characteristic properties which are common to all varieties of porcelain and china.

CHAPTER XLIII

GLASS

THERE are few substances that have contributed so much as glass to the comfort and convenience of civilized life, as well as to the development of scientific knowledge. From the common tumbler or milk bottle to the accurately ground lens of the microscope or telescope, the range of useful articles made from glass is very large and is constantly increasing.

463. Nature and Varieties of Glass. — Glass may be regarded as a solid solution of various silicates. By this we mean that the materials used in glass making are converted in the furnace into a mixture of liquid silicates, which on cooling gradually change from a liquid condition through a pasty state into a solid mass, much as melted wax does on standing in the air. Properly made glass shows no trace of crystalline or other regular structure, but is a hard, generally transparent mass, the shape of which depends upon the conditions under which it has solidified.

While there are a great number of special glasses designed for particular uses, it is much easier to classify the chief commercial varieties of glass than those of porcelain or earthenware. There is always present at least one alkaline (sodium or potassium) silicate, together with silicates of one or more of the metals calcium, barium, magnesium, lead, iron, aluminum, etc. Common *window* or *bottle* glass consists chiefly of sodium and calcium silicates ; *Bohemian* glass, much used for chemical glassware, is a potassium calcium glass; *flint* glass is a potassium lead glass. In addition to these chief varieties, there are a great number of varieties of special glass.

464. Materials for Glass Making. — The one essential constituent for all varieties of glass is "glass sand," which furnishes the silica (SiO_2). Only the cleanest and whitest of pure quartz sand can be used in making the best grades of glass, but in cheap varieties, where freedom from color is not essential, sand containing small amounts of iron or other impurities is sometimes employed. Sodium sulphate is used in the manufacture of the cheaper grades of glass, but for the best quality sodium carbonate is employed, as it can be obtained in a purer state. Potassium carbonate furnishes the potassium for the potash glasses. Limestone is the material most commonly employed to furnish calcium for glass. Many limestones consist of practically pure calcium carbonate and so can be used in making the best glass. The limestone should be as free as possible from magnesia, and if white (colorless) glass is to be made, it should contain very little iron — less than 1 %.

When glass is to contain barium in place of calcium, either a natural carbonate (witherite) or an artificially prepared carbonate is used. Flint glass, used for cut glass and for optical purposes, contains lead in place of calcium or barium. The lead compound chosen is either red lead, composed of PbO and PbO_2, or litharge (PbO). The red lead can be obtained free from impurities, but as it varies somewhat in the proportion of the oxides present, an analysis is usually made, to determine the proportion of it to be introduced into the mixture. While a large number of other materials are used in glass manufacture, either as constituents added to secure particular properties, or as a means of eliminating impurities in the basic materials, the raw materials for the chief varieties of glass are as follows:

Window glass — sand, sodium carbonate or sodium sulphate, limestone.

Bohemian glass — sand, potassium carbonate, limestone.

Flint glass — sand, potassium carbonate, red lead (or sometimes barium carbonate instead).

465. Action in the Glass Furnace. — An examination of the materials just named shows that in each case they consist of silica and basic oxides, or compounds easily reduced to basic oxides. In order that these materials may react to form silicates of the metals present, they must be ground fine, intimately mixed, and then raised to a temperature at which they will fuse together. When at this high temperature, silica, SiO_2, reacts with the alkaline carbonates to form silicates, with the liberation of carbon dioxide. A typical reaction would be:

$$\underset{\text{silicon dioxide}}{SiO_2} + \underset{\text{sodium carbonate}}{Na_2CO_3} \longrightarrow \underset{\text{sodium silicate}}{Na_2SiO_3} + \underset{\text{carbon dioxide}}{CO_2}$$

Silicates of the other metals are formed by similar reactions. The fact that the materials may be used in different proportions and the resulting substance still be recognized as glass, shows that the molten mass is essentially similar to a solution of two miscible liquids, such as alcohol and water.

The intimate mixing of the melted materials is greatly aided by the bubbles of carbon dioxide, as they pass up through the viscous mass. The temperature of the furnace and other conditions are so regulated as to secure as large bubbles as possible. If the bubbles are too small, the glass will not become sufficiently fluid to allow them to escape, so they will remain as flaws in the finished glass.

466. Structure of Glass Furnaces. — Two types of furnaces are used in glass manufacture, according to the use for which the glass is intended and the quantity to be made at a time. In the earlier type, the *pot furnace*, the materials were melted in fire-clay pots, holding from 400 to 4000 pounds of glass. The molding, drying, and first heating of these pots is a delicate operation requiring many weeks for its completion; after the pots have reached the full heat of the furnace, they are never allowed to cool until it is necessary to replace them. The clay employed must be able to stand extremely high temperatures without fusing, and must react only slightly with the glass in the pot. For fine grades of glass the pot is covered and its only opening is to the outside of the furnace (Fig. 164). The pots are usually arranged in a circle, walled about and roofed over with fire bricks (Fig. 165). The furnace is heated by the burning of a mixture of gas and air, which has been previously

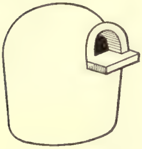


Fig. 164.

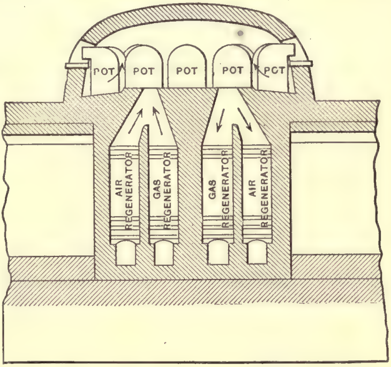

POT
POT
POT
POT
POT
AIR REGENERATOR
GAS REGENERATOR
GAS REGENERATOR
AIR REGENERATOR

Fig. 165. — Regenerative Pot Furnace.

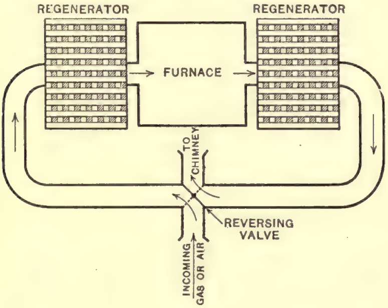

REGENERATOR
REGENERATOR
FURNACE
TO CHIMNEY
REVERSING VALVE
INCOMING GAS OR AIR

Fig. 166. — Regenerators for Heating Glass Furnace.

heated by passing through a hot checkerwork of bricks, like that employed in the open-hearth furnace for steel (Fig. 166).

The *tank furnace* (Fig. 167), used for the manufacture of bottle, plate, and sheet glass, is built up of blocks of fire clay, supported on a suitable steel frame, and cemented together by the glass which flows into the cracks from the first melt made in the furnace. It is roofed over in the same way as the pot furnace and heated by gas flames entering at the side or end. This furnace is continuous in operation, as the raw material is charged at one end and the finished glass is removed and worked at the other end.

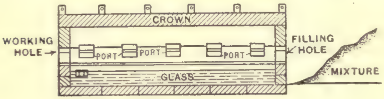


FIG. 167. — TANK FURNACE.

467. Chemical Properties of Glass. — We are accustomed to consider glass as a stable substance, unaffected by atmospheric agents or by ordinary chemicals. This is far from being the case, as a comparison of old windowpanes with new ones, or new bottles with those which have contained "ammonia" or other alkaline solutions, will show. Even with the most skilfully prepared glass mixtures, it is probable that there is an excess of some one or more of the constituents in the finished glass. If this excess material is an alkali, it will react with the carbon dioxide of the air to form minute crystals of the corresponding alkaline carbonate. This action is of importance, since these crystals are very hard, and, if the glass is rubbed with a dry cloth, the surface of the glass is apt to be scratched by these crystals and dulled. As the alkaline carbonates are readily soluble in water, the use of a damp cloth will prevent the injury of the surface by these crystals.

Water, as well as carbon dioxide, attacks the surface of glass by dissolving some of the soluble materials which happen to remain unaltered. In the case of strongly alkaline glass, the water may penetrate below the surface, and the surface layer may eventually scale off. The presence of specks of organic matter or finger marks increases the liability of glass to be attacked by both water and carbon dioxide. Eyeglasses and other lenses, for example, which are allowed to become dusty or finger-marked, frequently develop a permanent pitting of the surface under these marks.

The only acid having a marked affect on glass is hydrofluoric acid, HF. Like hydrochloric acid, this is a solution of a gas in water. Either the gas or the water solution will react with the silica of the glass, according to the equation :

$$\underset{\text{hydrofluoric acid}}{4\,\mathrm{HF}} + \underset{\text{silica}}{\mathrm{SiO_2}} \longrightarrow \underset{\text{silicon fluoride}}{\mathrm{SiF_4}} + \underset{\text{water}}{2\,\mathrm{H_2O}}$$

The silicon fluoride is soluble and can be removed by washing. It is necessary to keep hydrofluoric acid in paraffin or gutta percha bottles or in lead, as it would react with a glass bottle and be likely to eat its way through. The action just described is made use of in etching glass. When the etched portion is to be transparent, the solution of hydrofluoric acid is used ; and if the surface is to be dull, like ground glass, the gas is employed.

Strong alkalies, like sodium and potassium hydroxides, react with the silica of the bottles containing them, dulling the inner surface of the bottles and sometimes producing a sediment in the solution. Ammonium hydroxide acts in the same way, but to a less extent. Glass stoppers for alkali bottles should be covered with grease or paraffin, since the action of the alkali produces a cement that causes the stopper to stick.

468. Physical Properties of Glass. — Glass is always considered a hard material, but the different varieties show a great variation in this respect. In general, glass containing a large proportion of silica and lime is hard, while lead and barium glasses are much softer. In this connection it should be noted that flint glass is one of the softest varieties, the name being due to the former use of flints in the manufacture of this glass and not to the proverbial hardness of flint. The hardness of glass, like that of steel, depends upon the heat treatment it has received. Sudden cooling increases the hardness and brittleness; while slow cooling gives the glass a softer surface, but greater ability to resist shock and sudden changes of temperature. Securing proper heat resistance for glass is of great importance, as glass is a poor conductor of heat and therefore very liable to crack if unequally heated, particularly if the process of manufacture has left the glass with internal strains.

To relieve these internal strains and increase both the mechanical and heat resistance, nearly all varieties of glass are *annealed* before being given their final form. The annealing ovens are so arranged that the temperature of the glass is changed very gradually from a point just below the temperature at which it softens to the temperature of the outside air. The usual arrangement is a platform, on which the glass is placed and slowly moved through a long chamber, which is hot at the entrance and whose temperature gradually decreases to the exit. The passage through this furnace consumes hours, or even days, for the most carefully annealed glass. In special cases, other means of securing slow cooling are employed.

469. Aging of Glass. — Years of exposure to light produce color changes in glass; uncolored glass becomes purplish in tinge and the tints of colored glass change to a certain extent. Glass, on standing, also tends to lose its uniform structure and to become finely crystalline throughout. Such glass is unsuitable for the manufacture of chemical apparatus.

470. Manufacture of Commercial Forms. — The majority of glass objects are made by either blowing or pressing, or by a combination of these processes. *Window glass* may be taken as a typical illustration of the blowing process. A mass of the pasty glass is "gathered" by rotating the end of an iron blowpipe in the furnace. The blowpipe is then removed from the furnace, and by a combination of swinging, rotating, and blowing, with a softening of the glass by reheating when necessary, the glass is made to assume successively the forms shown in Fig. 168. The weight of the glass, the centrifugal force, and the pressure of the air within aid in the process. The end of the final cylinder is softened by heating, and a rapid rotation of the cylinder on its own axis causes the end to open out. The blowpipe is then detached from the glass, and a crack made

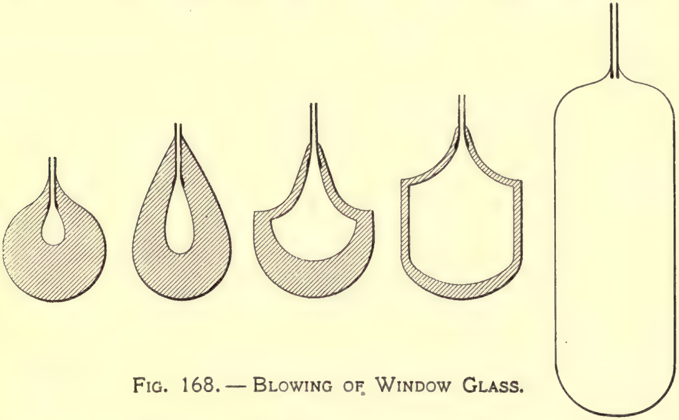


Fig. 168. — Blowing of Window Glass.

lengthwise in the cylinder. The split cylinder is now laid on a heated slab and gently flattened out, and finally passed into the annealing oven. It will be readily seen that any bubbles inclosed in the original gathering of glass will appear in the finished sheet, and that uneven heating, or irregular rotation, or variations in the composition of the gathering, will produce the streaks and other irregularities so commonly seen in window panes.

A combination of blowing, shaping with tools, and trimming is used in the production of the smaller articles of glassware. The steps in the evolution of a blown *tumbler* will be evident from Fig. 169. Thick tumblers are pressed. *Bottles*, electric light bulbs, and many other articles which could not conveniently be completely molded, are blown in molds (Fig. 170). In the case of bottles, automatic machinery and compressed air are employed to a considerable extent. *Pressed glass* is formed by compressing a mass of viscous glass between a plunger of the proper shape for the inside of the vessel and a mold. Much of the imitation cut glass is made in this

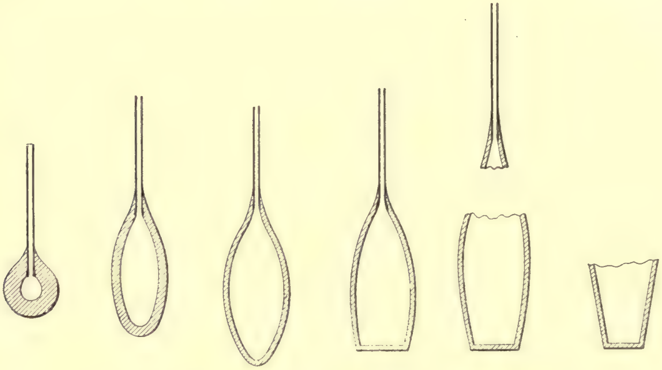
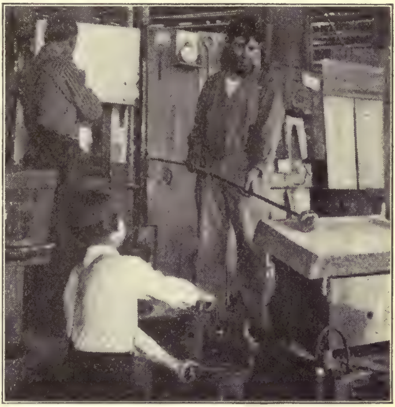


FIG. 169. — STEPS IN MAKING A GLASS TUMBLER.

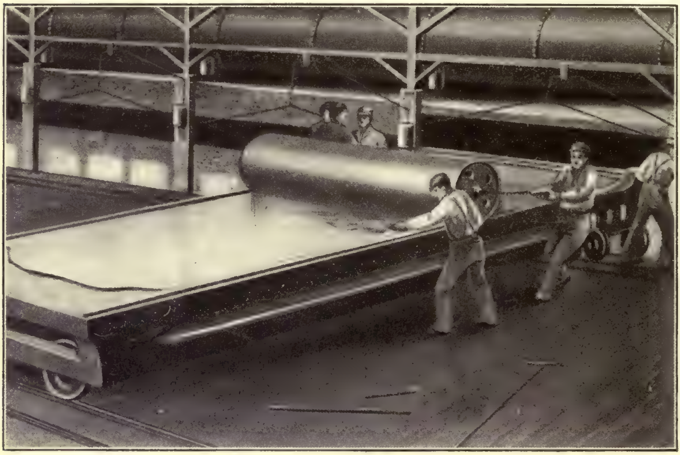
way; as pressed glass never has sharp edges, these are secured by slightly cutting on a wheel, or by means of hydrofluoric acid. True *cut glass* is made by first producing the desired shape in lead or barium glass, with thick walls, and then cutting in the design with a grinding wheel fed with water and emery powder. It will be readily seen that the amount of skilled labor required, and the unavoidable losses by breakage, together with a higher first cost for material, combine to make genuine cut glass expensive. In making *tubing*, the glass is gathered and a small cavity blown in the gathering. Another blowpipe is then attached to the opposite side of the gathering, and the two men holding the blowpipes move apart, one of them blowing, at a speed which depends on the size of the tubing to be made. By working in a tower one man may be dispensed with.



Copyright by the *Keystone View Co.*

FIG. 170. — DIPPING, MOLDING, AND FINISHING NECK OF BOTTLE IN THE MOLD (FOREGROUND).

The molten glass for *plate glass* is poured out on a table and spread out by a heavy roller, running on side rails of such a height from the table as to give the glass the desired thickness (Fig. 171). When the glass is hard enough to remove, it is placed in an annealing oven and annealed for from 4 to 5 days. It is ground first to a rough gray surface with sand, then to a smooth gray surface with a finer abrasive, and finally polished to a smooth, brilliant, perfectly level surface with rouge. Plate glass is made in sheets as large as 26 by 14 feet.



Courtesy of *The Scientific American.*

FIG. 171. — ROLLING OUT PLATE GLASS.

471. Optical Glass. — Glass for lenses, prisms, and other optical uses must possess chemical stability to a very high degree, it must be free from internal strains, and each piece must be of uniform composition throughout. The necessity of avoiding dust and finger marks, and the importance of cleaning lenses with a *damp* cloth have already been referred to (§ 467). These precautions are particularly important because, in general, the higher the refracting power of glass, the softer the glass. A great variety of materials have been tried in the endeavor to secure particular optical properties. To secure freedom from color effects, it is necessary to use compound lenses of at least two kinds of glass. Single lenses are usually made of crown glass, a colorless glass resembling window glass in composition. The glass used for color correction is a variety of flint glass, and concave lenses of this material are combined with convex crown glass lenses.

For optical glass, great care is taken in the selection of the materials, in the manufacture of the covered melting pot, and in the furnace treatment, so as to secure perfectly uniform, colorless glass, free from bubbles and other imperfections. When the melt is complete, the glass is allowed to solidify in the pot. In so doing, it commonly cracks up into irregularly shaped lumps. The pot is broken away, the lumps sorted, and the best ones set aside for lenses. These selected pieces are then softened by heat, and each pressed into a mold of the approximate shape of the lens to be made. The blanks thus secured are then ground by rubbing against surfaces of the proper curvature, and carefully polished to the exact shape desired. As only a single piece can be used for one lens, the difficulty in securing a blank for a large lens is enormous. At best, only from 10 % to 20 % of the yield of optical glass is available for lenses of any size.

472. Colored Glass. — Color in glass may result from dissolved compounds, as, for example, the iron compounds which are present in green bottle glass; or from finely divided particles. Ruby glass is an example of the latter method of coloring, owing its color to extremely fine particles of gold or of cuprous oxide. Great care must be taken in coloring of this sort to secure particles of the proper size. By varying the rate of cooling, visible particles, such as the shimmering flakes seen in some glass marbles, are produced. Where an intense color is produced by a dissolved compound, as in cobalt blue glass, lighter shades are obtained by "flashing." This consists of coating white — colorless — glass with a thin sheet of the blue, and then heating until the two sheets amalgamate. The same result may be attained by two gatherings, the first of the colorless and the second of the colored glass. *Stained* glass is made by the use of very fusible surface glazes, which are then fired in a kiln at a temperature high enough to fuse the glaze, but not high enough to soften the body of the glass.

Materials are often added to a mixture of ordinary glass materials to furnish a color complementary to that produced by some impurity already present in the mixture, and thus produce a colorless glass. The purple which manganese would produce alone is thus used to neutralize the greenish tinge which iron would produce. The following table gives the colors and the metals whose oxides or salts are commonly used to produce them. By proper combinations, almost any color may be produced, but the results in making colored glass are always somewhat uncertain, because of the modifications that the heat treatment employed may produce.

COLOR	METAL WHOSE COMPOUNDS ARE USED
Red.	Cuprous oxide, with or without tin oxide; gold.
Pink.	Selenium, in lead or barium glass.
Yellow.	Carbon (finely divided); uranium (fluorescent glass); silver, as surface stain only.
Brown.	Nickel; carbon (finely divided); manganese and iron.
Green.	Chromium; iron.
Blue.	Cobalt.
Purple.	Manganese.
White.	Tin oxide; aluminum fluoride (opalescent).

473. Chemical Glassware. — Several kinds of glassware are used in chemical laboratories and industries. For articles such as test tubes, bottles, and ordinary glass tubing, which are not designed to be heated to a high temperature, a good soda-lime glass, similar to window glass, is employed. *Combustion*, or hard-glass, tubing, in which solids are to be intensely heated, is made of Bohemian glass, a potash-lime glass, containing a large proportion of lime. Laboratory flasks also are usually made of this glass. During recent years, this combustion tubing has been largely replaced by *Jena combustion tubing.* This is made at a factory in Jena, Germany, at which a very thorough study has been made of the relation between the composition of glass and its properties, with the result that this factory turns out a great many varieties of glass adapted to special uses. The Jena combustion tubing contains a considerable amount of boron and some magnesium. It will sustain a very high temperature without softening, and is less liable to crack with sudden changes of temperature than ordinary hard glass. It has the disadvantage of growing gradually milky in appearance with repeated heating, and finally becomes practically opaque on this account.

474. Silica Ware. — The development of high temperature gas and electric furnaces has made possible the manufacture of a remarkable substitute for glass. This is vitrified silica; that is, pure silicon dioxide made plastic by intense heat and fashioned into laboratory ware. When quartz is thus softened by an oxy-hydrogen or oxy-acetylene blowpipe, the result is a *transparent* silica ware, resembling glass in appearance. Vitrified silica expands much less than glass when heated and conducts heat much better. On this account, it can stand sudden changes in temperature much better than Jena glass. A white-hot silica dish can be plunged into cold water without cracking. The difficulties of manufacture limit the size of transparent silica articles and make the price high.

When silica is fused in an electric furnace, gas bubbles appear, similar to those formed when glass is melted. These bubbles do not readily escape, and when articles are made of this silica, the bubbles are drawn out into tiny tubes in the silica and give it a milky appearance (Fig. 172). This *opaque* silica has properties similar to the transparent silica, except that chemical action in an opaque silica tube cannot be watched like that in transparent silica. The transparent silica has certain optical uses for lenses and vacuum tubes which will transmit ultra-violet light, for which naturally the milky silica cannot be used. The electric furnace product is much cheaper than the transparent silica.

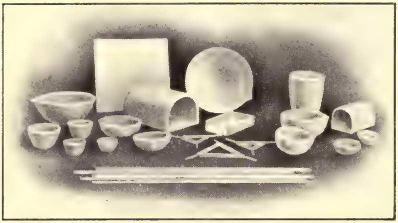


FIG. 172. — LABORATORY SILICA WARE.

Silica ware, being composed of an acid anhydride, is very rapidly attacked by alkalies, and should never be used to contain an alkaline solution or a solid alkali. At or above red heat, silica is a strongly acid material in its reactions, and on this account is unsuitable for the fusion of metals.

The high and definite melting point of vitrified silica makes it valuable for tubes in electric laboratory furnaces, as it can be heated to very high temperatures without danger of melting.

The lightest fibers used to support the parts of delicate instruments are made of quartz. The quartz is softened with an oxygen blast lamp, the end of an arrow dipped in it and quickly shot from a bow down a long passage. The most difficult part of the operation is to find the tiny fiber, and to pick it up without breaking it.

SUMMARY

Glass is a solid solution of silicates.

Window Glass consists chiefly of sodium and calcium silicates.

Bohemian Glass consists chiefly of potassium and calcium silicates.

Flint Glass consists chiefly of potassium and lead or barium silicates.

The Materials used in glass manufacture are chiefly glass sand, sodium carbonate, potassium carbonate, limestone, barium carbonate, red lead, and litharge.

Manufacture. — The materials chosen for a particular glass are ground, intimately mixed, and heated in a fire-clay pot until they fuse and react. In making bottle, plate, or sheet glass, a tank furnace is used. Glass furnaces are heated by gas. Window glass is blown in cylinders and then flattened out. Bottles and many other articles are blown in molds. Plate glass is rolled out, and then ground to a plane surface. Glass is annealed by slow cooling, to prevent internal strains.

Properties. — Glass is slightly soluble in water, and reacts with carbon dioxide and alkalies. Lead and barium glasses are softer than other varieties.

Glass is Etched with hydrofluoric acid, as this forms a gaseous compound with the silica as well as certain soluble fluorides.

Optical Glass is made of special materials, and requires the greatest care in manufacture.

Colored Glass contains dissolved metallic compounds. Stained glass has a colored surface glaze only.

Combustion Tubing, or hard glass, is either Bohemian glass or Jena glass. The Jena tubing will stand higher temperatures, but becomes opaque on repeated heating.

Silica may be fused by the oxy-hydrogen blowpipe or the electric furnace. Silica ware withstands high temperatures and sudden changes of temperature. Alkalies should never be placed in silica ware.

EXERCISES

1. Give the essential composition of glass.

2. Distinguish between window glass, Bohemian glass, and flint glass.

3. State what you understand by a solid solution.

4. Give the materials used and describe the manufacture of some one kind of glass.

5. Compare pot and tank furnaces as to (*a*) construction, (*b*) relative advantages, (*c*) kind of glass for which each is used.

6. Explain, using an equation, the production of carbon dioxide in glass making and state how it is eliminated from the finished glass.

7. Why should cut glass be cleaned with a soft cloth and water that is warm, but not hot?

8. State the proper method of cleaning lenses.

9. State the effect on glass of each of the following: air; water; alkalies; hydrofluoric acid; other acids.

10. Describe the process of annealing glass and state its effect on the properties of the glass.

11. Explain the presence of (*a*) bubbles, (*b*) streaks, (*c*) opaque particles in window glass.

12. Why is ruby glass commonly "flashed"?

13. Name two properties particularly desirable in optical glass and state how these are secured.

14. Give two reasons why plate glass is more expensive than ordinary window glass.

15. Name three kinds of glass used for chemical ware.

16. Show how the differences in the properties of the three kinds of chemical glassware fit them for their particular uses.

17. What is "vitrified silica" and how is it made?

18. In what respects is vitrified silica superior to glass? Why does it not replace glass entirely?

19. What precaution must be taken in the use of a silica crucible?

CHAPTER XLIV

COMMERCIAL CHEMICALS

475. Purity of Chemicals. — In the last fifteen years this country has made a marked advance in the manufacture of chemicals. Formerly there were practically but two grades, *commercial* and *C. P.* (chemically pure). The commercial grade was the crude quality suitable for technical purposes, where small amounts of other compounds as impurities did not greatly interfere with the particular use of the chemical. Chemically pure chemicals were used by druggists and for the more exacting requirements of the chemical laboratory. Unfortunately, "C. P." did not always insure absence of impurities. To meet the demand for chemicals of undoubted purity, several firms began to analyze each lot of their products and place the analysis on the label. These *analyzed chemicals* of tested purity have been a great aid to accurate analytical work, which is, after

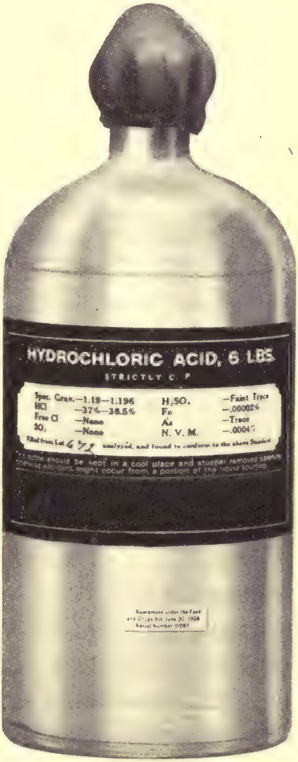

HYDROCHLORIC ACID, 6 LBS
STRICTLY C. P.
Spec. Grav.—1.19—1.196
HCl —37%—38.5%
Free Cl —None
SO₃ —None
H₂SO₄ —Faint Trace
Fe —.00002%
As —Trace
N. V. M. —.0004%
Filled from Lot 672 analyzed, and found to conform to the above Standard

FIG. 173. — ANALYZED CHEMICAL.

all, the regulating factor in chemical industries and most useful in chemical education and research. Testing for impurities, better knowledge of the theory of solutions, and improved chemical machinery, such as separators, evaporating pans and centrifuges, have enabled manufacturers to place chemicals of high purity on the market at a very reasonable price.

To-day the listed grades of chemicals are *crude*, *technical*, *C. P.*, and *analyzed*. The technical quality is suitable for most industrial purposes and the C. P. grade from a reliable manufacturer serves well the ordinary purposes of the chemical laboratory. It is only a question of time, however, when the C. P. grade will be replaced by analyzed chemicals.

HYDROCHLORIC ACID

476. Manufacture. — The manufacture of hydrochloric acid grew out of the manufacture of "salt cake" (sodium sulphate), made by heating common salt with concentrated sulphuric acid. The gaseous product, hydrogen chloride, once allowed to escape into the air, is now more valuable than the salt cake.

The reaction takes place in two stages :

$$\underset{\text{sodium chloride}}{NaCl} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{sodium bisulphate}}{NaHSO_4} + \underset{\text{hydrogen chloride}}{HCl}$$

$$\underset{\text{sodium bisulphate}}{NaHSO_4} + \underset{\text{sodium chloride}}{NaCl} \longrightarrow \underset{\text{sodium sulphate}}{Na_2SO_4} + \underset{\text{hydrogen chloride}}{HCl}$$

The first action takes place at ordinary temperatures, but commercially it usually occurs in a warm part of the furnace. Then the cast iron retorts containing the mixture are pushed into a hot muffle or upon the bed of a reverberatory furnace, where the second reaction is completed. Purer acid is obtained from the first action than from the second. Accordingly there is a separate set of condensers and absorbers for the two grades of acid.

The hydrogen chloride gas is led through long cooling pipes, then through a series of earthenware Woulff bottles, and finally into the bottom of tall, narrow towers filled with coke, over which water flows, in order to complete the absorption of the hydrogen chloride begun in the Woulff bottles. The dilute hydrochloric acid obtained from the coke towers furnishes the absorbing liquid for the Woulff bottles and circulates through them. In this way a concentrated acid is obtained, the most concentrated coming from the bottles nearest the furnace.

477. Properties of Hydrochloric Acid. — The ordinary C. P. concentrated hydrochloric acid has a specific gravity of 1.20 and contains about 40 % by weight of dissolved hydrogen chloride gas. *Commercial* hydrochloric acid is impure, and its yellow color may be due to traces of iron, free chlorine, or organic matter. It is commonly called *muriatic acid.*

When a bottle of concentrated hydrochloric acid is opened to the air, white fumes are often seen. This fuming is due to gaseous hydrogen chloride dissolving in the water vapor of the air. The solution thus formed condenses to a white mist composed of tiny liquid particles of hydrochloric acid.

Hydrochloric acid does not react with noble metals, like gold and platinum, and but slightly affects copper. With lead, silver, and mercury, its action is also slight, as these metals form insoluble chlorides. It is, however, a very active acid, dissolving most other metals with the liberation of hydrogen and the formation of salts (§ 14). Like all strong acids, it reacts vigorously with bases and with most metallic oxides and decomposes the salts of less active acids. Although minute quantities of hydrochloric acid are found in the gastric juice and are essential to good digestion, the acid is an active poison.

478. Uses of Hydrochloric Acid. — This acid has a wide range of industrial uses. Among the most important are the "pickling" of iron before tinning, the preparation of chlorides, the production of chlorine used for bleaching powder manufacture, and the manufacture of glue and gelatine.

NITRIC ACID

479. Manufacture. — The process most used in this country for making nitric acid is based upon the following reaction :

$$\underset{\text{sodium nitrate}}{NaNO_3} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{sodium bisulphate}}{NaHSO_4} + \underset{\text{nitric acid}}{HNO_3}$$

The mixture of niter and sulphuric acid is heated in an iron retort at a carefully regulated temperature, so as not to decompose the nitric acid formed and to prevent other undesirable reactions from occurring. The distillation is stopped before all the sulphuric acid is used, so that the "niter cake" left in the retorts may be easily removed. This niter cake is used for other purposes.

The gaseous nitric acid is cooled in a series of condensers. The liquid obtained has a yellowish tinge, due to dissolved oxides of nitrogen formed by the decomposition of a little of the nitric acid in the process of distillation. It may also contain chlorine if the niter contained any salt.

To decolorize ("bleach") the condensed acid, air is blown through it, thus liberating the gaseous impurities. The oxygen of the air converts the lower oxides of nitrogen into the higher ones, which are absorbed by the water with the formation of more nitric acid. The actual process is an ingenious but complicated one.

480. Packing and Storage of Nitric Acid. — Concentrated nitric acid of commerce has a specific gravity of 1.42 and contains about 70 % by weight of hydrogen nitrate, HNO_3. It is stored in stone pots, but is commonly shipped either in carboys containing about 120 pounds of the acid, or in 7 pound glass-stoppered bottles. On account of the powerful oxidizing action of nitric acid, it should never be allowed to come in contact with inflammable material such as straw or wood. Neither should nitric acid be stored near easily oxidizable chemicals, as an oxidizing agent and a combustible material near together form a source of great danger if a fire starts.

481. Properties of Nitric Acid. — Pure hydrogen nitrate, HNO_3, is a colorless liquid, boiling at 86° C. Nitric acid is the water solution of this compound and its boiling point depends upon the amount of dilution. A solution containing 68 % of hydrogen nitrate boils constantly at 120° C.

When concentrated nitric acid is heated, the following decomposition occurs:

$$\underset{\text{nitric acid}}{4\,HNO_3} \longrightarrow \underset{\text{water}}{2\,H_2O} + \underset{\substack{\text{nitrogen}\\ \text{peroxide}}}{4\,NO_2} + \underset{\text{oxygen}}{O_2}$$

Sunlight also causes this reaction. Bottles of the acid standing near windows often become yellowish red, on account of the red nitrogen peroxide liberated in the liquid.

Nitric acid is one of the most active acids. It reacts readily with most metals, but attacks neither platinum nor gold. Imitation gold jewelry is often detected by putting a drop of the concentrated acid upon it. Unlike many acids, hydrogen is seldom obtained by the reaction of nitric acid with metals. The hydrogen at the moment of its liberation is oxidized to water by oxygen from other nitric acid molecules. When the acid is very concentrated, the following reaction occurs with most metals:

$$\underset{\text{nascent hydrogen}}{H} + \underset{\text{nitric acid}}{HNO_3} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\text{nitrogen peroxide}}{NO_2}$$

When the acid is somewhat diluted, nitric oxide is frequently obtained:

$$\underset{\text{nascent hydrogen}}{3\,H} + \underset{\text{nitric acid}}{HNO_3} \longrightarrow \underset{\text{water}}{2\,H_2O} + \underset{\text{nitric oxide}}{NO}$$

Certain concentrations may give a mixture of the nitric oxide and the nitrogen peroxide. These compounds are called *reduction products* of nitric acid, as they are formed as a result of nascent hydrogen taking oxygen away from the acid molecule. With very dilute nitric acid, the reduction product may be ammonia, which would unite with the excess of nitric acid present to form ammonium nitrate. The reaction which takes place between nitric acid and a metal depends upon the metal used, the concentration of the acid, and the temperature.

It is to be remembered, then, that nitric acid very rarely gives hydrogen when reacting with a metal, as the oxidizing action of the acid converts the hydrogen into water. The oxidizing power of nitric acid is shown in many other reactions. Hot charcoal burns in the hot concentrated acid, an ordinary gas flame burns readily in the hot acid vapor; most organic compounds are vigorously attacked by nitric acid. The concentrated acid makes holes in clothing and makes yellow spots on the skin.

482. Uses of Nitric Acid. — The acid is of great industrial importance, particularly in the manufacture of nitroglycerine, gun cotton, smokeless powder, celluloid, and many other organic compounds. Its salts are important as fertilizers, in electroplating, and in the manufacture of fireworks.

An important laboratory use is in *aqua regia*, a mixture of three parts by volume of concentrated hydrochloric acid to one part of concentrated nitric acid. This mixture dissolves gold and platinum, owing to the liberation of nascent chlorine due to the oxidizing action of nitric acid:

$$\underset{\text{hydrochloric acid}}{3\,HCl} + \underset{\text{nitric acid}}{HNO_3} \longrightarrow \underset{\text{nascent chloride}}{3\,Cl} + \underset{\text{water}}{2\,H_2O} + \underset{\text{nitric oxide}}{NO}$$

483. Nitric Acid from the Air. — The formation of nitric acid and nitrates by the fixation of atmospheric nitrogen is discussed in Chapter XLVI, § 513. By this method, nitrogen and oxygen of the air are combined by means of the electric arc. A number of processes based upon this principle have been devised, but it appears at present that none of them will be able to compete in the production of *concentrated* nitric acid, unless the manufacturer has abundant water power at his disposal for the cheap production of electricity. The process is, however, a commercial success in producing *dilute* nitric acid and particularly a supply of *calcium nitrate*, a most valuable fertilizer. Until the great niter beds of Chili are exhausted, a large part of the world's concentrated nitric acid will be made from sodium nitrate.

SULPHURIC ACID

484. Manufacture by Contact Process. — This process is based upon four reactions: the burning of sulphur; the oxidation, by a catalytic agent, of the sulphur dioxide to sulphur trioxide; the absorption of the sulphur trioxide by concentrated sulphuric acid; and finally the dilution of the last product with water:

$$\underset{\text{sulphur}}{S} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{sulphur dioxide}}{SO_2}$$

$$\underset{\text{sulphur dioxide}}{2\,SO_2} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{sulphur trioxide}}{2\,SO_3}$$

$$\underset{\text{sulphur trioxide}}{SO_3} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow H_2SO_4 \cdot SO_3$$

$$H_2SO_4 \cdot SO_3 + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{sulphuric acid}}{2\,H_2SO_4}$$

Instead of making use of the last two steps, it might be thought that sulphur trioxide could be absorbed directly by water:

$$\underset{\text{water}}{H_2O} + \underset{\text{sulphur trioxide}}{SO_3} \longrightarrow \underset{\text{sulphuric acid}}{H_2SO_4}$$

In practice, however, it has been found that the sulphur trioxide formed by the contact process is not readily soluble in water.

485. Development of the Contact Process. — The contact process has been known for a hundred years, but only within the past 20 years has it become a commercial success. Certain difficulties had to be overcome before the laboratory reactions could be conducted profitably on a manufacturing scale.

For a long time the necessity for an excess of air (oxygen) was not recognized. Secondly, in the laboratory the union of sulphur dioxide and oxygen took place almost completely, while in the factory it was found that after a time the platinum lost its effectiveness as a contact agent. This poisoning of the platinum was found to be due to the action of arsenic trioxide and other compounds present as impurities in the sulphur dioxide gas. It was necessary to devise means of removing these before admitting the gas to the contact chambers. Finally came the recognition of the necessity for careful regulation of the temperature, as the following reaction is reversible:

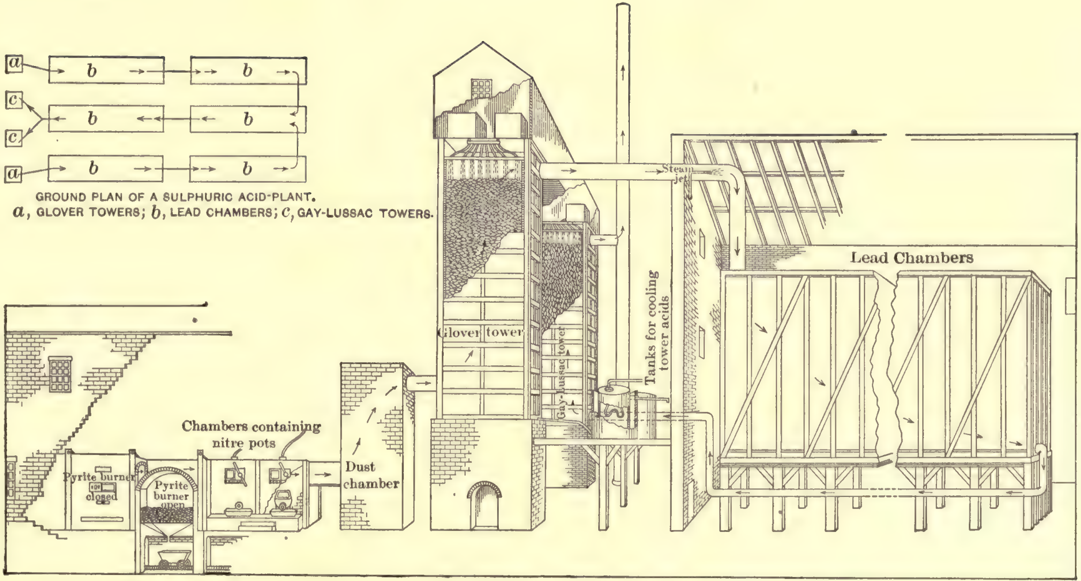
$$\underset{\text{sulphur dioxide}}{2\,SO_2} + \underset{\text{oxygen}}{O_2} \rightleftarrows \underset{\text{sulphur trioxide}}{2\,SO_3}$$

The catalytic union of the dioxide and oxygen takes place most completely between 400° C. and 450° C. At higher temperatures the reaction tends to proceed in the opposite direction. Moreover the union of the dioxide and oxygen produces heat. This difficulty was solved by using this heat to bring the incoming gases to the proper reaction temperature.

486. Manufacture by Chamber Process. — For more than a century all of the sulphuric acid used for commercial purposes was made by the chamber process. To-day, owing to patents on the most approved forms of apparatus for carrying on the contact process, and to the fact that manufacturers dislike to abandon expensive equipment in good working order, the chamber process is still very extensively used for the manufacture of commercial oil of vitriol. The commercial acid produced by this process is not pure and is not concentrated. It contains only about 60 % to 70 % of sulphuric acid. The advantage of the contact process over the chamber process is that the former directly produces a concentrated, pure acid.

The sulphur dioxide used in the manufacture of sulphuric acid is often obtained by heating in contact with air some sulphide of a metal, usually iron sulphide (pyrites). The sulphur dioxide is converted into the higher oxide by making use of nitrogen peroxide. The peroxide is obtained by the action of air with nitric oxide:

$$\underset{\substack{\text{nitric}\\ \text{oxide}}}{2\,NO} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{nitrogen}\\ \text{peroxide}}}{2\,NO_2}$$


a
c
c
a
b
b
b
b
b
b
Lead Chambers
Steam jet
Glover tower
Gay-Lussac tower
Tanks for cooling tower acids
Dust chamber
Chambers containing nitre pots
Pyrite burner closed
Pyrite burner open

GROUND PLAN OF A SULPHURIC ACID-PLANT.
a, GLOVER TOWERS; *b*, LEAD CHAMBERS; *c*, GAY-LUSSAC TOWERS.

FIG. 174.—CHAMBER PROCESS FOR MAKING SULPHURIC ACID.

The nitric oxide results from the reaction of nitric acid with water and sulphur dioxide. The nitric acid is made by the action of sulphuric acid with sodium nitrate in vessels called niter pots.

Sulphur dioxide mixed with nitrogen peroxide is passed through a tower called the Glover tower, to be described later, and then into large lead chambers. Within the chambers sulphur dioxide, nitric oxide, nitrogen peroxide, air, and steam are brought together. Complicated reactions take place which are not well understood.

Since approximately four-fifths of the air is nitrogen, it is necessary to provide for the escape of the nitrogen and at the same time prevent the escape of the oxides of nitrogen as far as possible. This is accomplished by causing the chamber gases to pass through the Gay-Lussac tower. The tower is filled with coke. Concentrated sulphuric acid (78 % H_2SO_4) is conveyed to the top of the tower and sprinkled on the coke. The chamber gases enter the tower at the bottom and ascend against the stream of sulphuric acid. When the plant is running properly, practically all of the oxides of nitrogen are dissolved in the sulphuric acid. In this manner they are caught in the Gay-Lussac tower, while the nitrogen, being insoluble in the acid, escapes.

From the bottom of the Gay-Lussac tower the sulphuric acid, carrying in solution the oxides of nitrogen, is pumped to a tank on the top of another tower, called the Glover tower, situated between the ore roasters and the chambers. The Glover tower is similar in construction to the Gay-Lussac tower. It is filled with lumps of quartz. At the top of the tower are two tanks, one containing the liquid coming from the Gay-Lussac tower, and the other the chamber acid (55 % H_2SO_4). As a mixture of these two liquids passes down through the Glover tower, it meets the hot gases coming from the ore roasters and from the nitric acid plant, on their way to the lead chambers. The result is that the dilute chamber acid is made more concentrated, the Gay-Lussac acid is decomposed by the water in the chamber acid, and the oxides of nitrogen liberated are allowed to enter the chambers, while sulphuric acid (67 %) is obtained from the bottom of the tower. This chamber acid can be concentrated by boiling in iron pans and then in platinum pans, but for many commercial purposes needs no further treatment.

487. Storage and Packing. — Concentrated sulphuric acid is usually stored in riveted steel tanks; the less concentrated grades are run into lead-lined wooden tanks. The acid is shipped in steel tank cars holding from 30 to 80 tons, or in steel drums containing from 500 to 1500 pounds. The smaller quantities for laboratory use are sent in carboys (large glass bottles packed in wooden cases) containing about 200 pounds.

488. Physical Properties. — Concentrated sulphuric acid is a heavy, oily liquid, nearly twice as dense as water. *Oil of vitriol* is the commercial name of the acid, derived from an early method of manufacture — distillation of green vitriol, $FeSO_4 . 7 H_2O$. The acid is miscible with water in all proportions, but great care must be taken in the mixing (§ 19). The high boiling point, 338° C., of sulphuric acid makes it valuable for use in the preparation of many other acids.

489. Chemical Properties. — In general, sulphuric acid is not so active an acid as hydrochloric acid or nitric acid. It reacts, however, with most metals, the rapidity of the action and the products formed depending upon the temperature, the metal, and the amount of water present.

Dilute sulphuric acid gives a sulphate and hydrogen with metals like iron and zinc:

$$\underset{\text{zinc}}{Zn} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{zinc sulphate}}{ZnSO_4} + \underset{\text{hydrogen}}{H_2}$$

The metals mercury, silver, and copper are practically unaffected by the dilute acid, but the hot, concentrated acid reacts with them so as to produce sulphur dioxide instead of hydrogen:

$$\underset{\text{copper}}{Cu} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{2\,H_2SO_4} \longrightarrow \underset{\substack{\text{copper}\\ \text{sulphate}}}{CuSO_4} + \underset{\substack{\text{sulphur}\\ \text{dioxide}}}{SO_2} + \underset{\text{water}}{2\,H_2O}$$

One explanation for this action is that the excess of hot concentrated acid oxidizes the hydrogen first formed by the interaction of metal and acid:

$$\underset{\text{copper}}{Cu} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{copper}\\ \text{sulphate}}}{CuSO_4} + \underset{\substack{\text{nascent}\\ \text{hydrogen}}}{2\,H}$$

$$\underset{\substack{\text{nascent}\\ \text{hydrogen}}}{2\,H} + \underset{\substack{\text{excess}\\ \text{of acid}}}{H_2SO_4} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\substack{\text{sulphurous}\\ \text{acid}}}{H_2SO_3}$$

The sulphurous acid formed breaks down in the hot solution into water and sulphur dioxide:

$$\underset{\substack{\text{sulphurous}\\ \text{acid}}}{H_2SO_3} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\substack{\text{sulphur}\\ \text{dioxide}}}{SO_2}$$

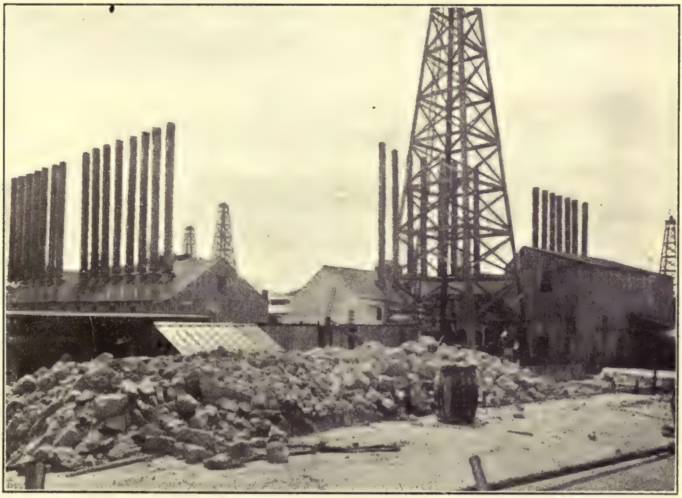
Sulphuric acid has a powerful *dehydrating action* on many compounds, by taking from them hydrogen and oxygen in the proportion in which these elements combine to form water. Thus with paper, wood, and sugar, the removal of the hydrogen and oxygen leaves a charred mass of carbon. The dehydrating action makes sulphuric acid burns very painful and dangerous. Many of the industrial uses of the acid depend upon its dehydrating action.

490. Uses. — Next to fertilizers, sulphuric acid is the chemical product of greatest value in this country. More than one hundred and fifty manufacturing plants are devoted to its production. By far the greatest quantity of the acid is used in the preparation of fertilizers, particularly phosphates and ammonium sulphate. The refining of petroleum consumes the next largest amount. Other important uses are the pickling of iron and steel, the preparation of sulphates, particularly aluminum sulphate, and, in connection with nitric acid, the manufacture of explosives. So varied are the uses of this acid that there is hardly an industry that does not depend directly or indirectly upon sulphuric acid or some product made with it.

SULPHUR

491. Extraction. — Sulphur is an element of great commercial value. Formerly the chief sources of native or uncombined sulphur were volcanic regions, particularly Sicily and Japan. In Sicily the rocky material containing the sulphur is heaped into piles, which are covered with spent ore, so that only sufficient air is admitted to burn a small portion of the sulphur. The sulphur that burns produces sufficient heat to melt the remainder of the sulphur, which runs out of the bottom of the pile into a collecting pool. This crude sulphur is purified by remelting in iron pots from which it is run into retorts, where it is vaporized. The vapor is passed into brick chambers, where it deposits on the cool walls as a fine powder, known as *flowers of sulphur*. Soon, however, the walls become warm and most of the vaporized sulphur condenses as a liquid, which makes its way to the outlet of the condensing chamber. It is then cast in wooden cylindrical molds. This form is *roll sulphur*, or brimstone.

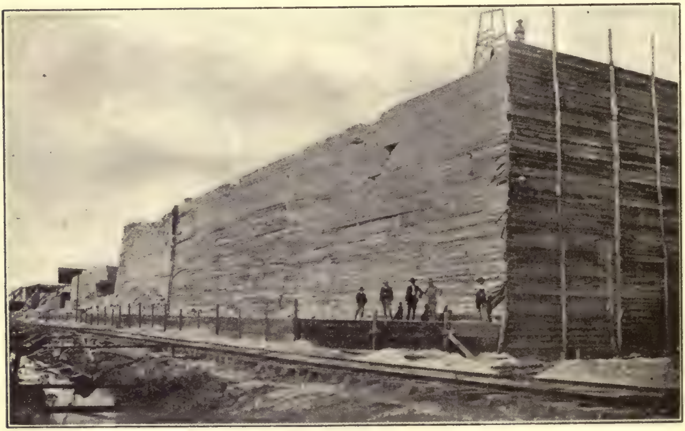
The sulphur used in this country is obtained almost entirely from the Louisiana deposits. These beds are about 500 feet below the surface. An Austrian, a French, and several American companies failed in their efforts to bring the sulphur to the surface on a profitable basis, on account of quicksands overlying the deposits. It remained for Herman Frasch, long distinguished as an oil chemist, to solve the problem in a most ingenious and scientific way.



Copyright by *The Scientific American.*

FIG. 175. — LOUISIANA SULPHUR WELL WITH ITS BATTERY OF BOILERS.

In the Frasch process, a hole is bored and piped down through the 500 feet of overlying deposits to the bottom of the sulphur bed, which is 200 feet more. Inside the large pipe casing of the hole for the entire distance is a 6-inch pipe, and inside this a 3-inch pipe, which in turn surrounds a 1-inch pipe for supplying hot compressed air. Through the 6-inch pipe water heated to 167° C. under a pressure of 100 lbs. is forced down the well to melt the sulphur below. The hot, compressed air mingles with the liquid sulphur and so reduces the specific gravity of the liquid to be raised to the surface. The combined pressure of the column of hot water and hot air raises the sulphur to the surface through the 3-inch pipe. Strainers at the bottom prevent the earthy material from being driven upward. On reaching the surface, the melted sulphur is run into huge bins 60 feet high, made of rough boards. The sulphur soon cools, forming an enormous block of solid sulphur of remarkable purity. Some of these blocks contain 100,000 tons of sulphur (Fig. 176). The block is broken by blasting and is loaded on cars by steam shovels.



Copyright by *The Scientific American.*

FIG. 176. — BLOCK OF LOUISIANA SULPHUR.

As the sulphur is pumped out, the overlying clay and sand tend to follow the settling of the sulphur rock. To prevent the breaking of the well pipes by the resulting strains, it was found necessary to protect them by casing the hole through the clay with a 12-inch pipe having telescoping joints. The sulphur obtained is over 99 % pure, and not only supplies the American market, but is shipped to Europe as well.

492. Uses of Sulphur. — Sulphur is used as a source of sulphur dioxide, to be employed for bleaching and disinfecting. Either the element, the monochloride of sulphur, or antimony sulphide, serves for the hardening (vulcanizing) of rubber. Sulphur is now less used for the manufacture of fireworks and gunpowder, but finds an increasing use in the manufacture of carbon disulphide and dyestuffs.

493. Ammonia. — The principal source of the ammonia of commerce is the ammoniacal liquid obtained in the destructive distillation of soft coal (Chap. XXXII). The improved ovens for the manufacture of coke provide for the recovery of the ammonia liberated in the process. The increasing demand, however, for ammonium salts as fertilizers has directed attention to the possibility of the synthesis of ammonia from the elements nitrogen and hydrogen:

$$\underset{\text{nitrogen}}{2\,N_2} + \underset{\text{hydrogen}}{3\,H_3} \rightleftarrows \underset{\text{ammonia}}{2\,NH_3}$$

The reaction is a reversible one, and the small yield of ammonia has been the bar to its development on a commercial scale.

It has been found, however, that by the use of a suitable catalytic agent and the regulation of temperature and pressure, synthetic ammonia can be made profitably. Iron and uranium are among the metals used as catalyzers. The best temperature range is between 500° C. and 700° C. and the pressure from 100 to 200 atmospheres. A mixture of 1 volume of nitrogen with 3 of hydrogen is passed over the catalytic agent in a furnace of special design. Then the hot gases are subjected to a low temperature, so as to liquefy the ammonia formed and to separate it from the nitrogen and hydrogen remaining uncombined.

Ammonia is sold in its water solution. The concentrated commercial article has a specific gravity of about 0.9 and contains almost 30% of the gas (NH_3). This water solution contains some of the ammonia in the form of ammonium hydroxide, but the larger portion is in physical solution. Household ammonia is supposed to contain 8 % NH_3, but the commercial article sometimes contains as low as 2 % of ammonia.

Ammonium hydroxide is an active alkali and, like sodium hydroxide, acts slowly upon glass. This accounts for the opaque appearance of the reagent bottles used for ammonium hydroxide in the laboratory.

Liquefied ammonia is the gas (NH_3) which has been reduced to a liquid by pressure. It is important in the manufacture of artificial ice and for use in refrigerating plants. In the latter, the cooling liquid circulating in the pipes is brine, which has been cooled by the evaporation of liquid ammonia.

494. Sodium and Potassium Carbonates.—These carbonates are made by the Solvay process, which is remarkable for the cheapness and efficiency of its operation. It is based on the reaction between sodium chloride and ammonium bicarbonate in cold solution. Ammonium bicarbonate may be made by the following reaction:

$$\underset{\text{ammonia}}{NH_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2} \longrightarrow \underset{\substack{\text{ammonium}\\\text{bicarbonate}}}{NH_4HCO_3}$$

The reaction for the double replacement of this compound with sodium chloride is:

$$\underset{\substack{\text{sodium}\\\text{chloride}}}{NaCl} + \underset{\substack{\text{ammonium}\\\text{bicarbonate}}}{NH_4HCO_3} \longrightarrow \underset{\substack{\text{sodium}\\\text{bicarbonate}}}{NaHCO_3} + \underset{\substack{\text{ammonium}\\\text{chloride}}}{NH_4Cl}$$

In the Solvay process, these reactions are not conducted in just this way, but they probably take place. A concentrated brine solution is saturated with ammonia gas in tanks with perforated false bottoms. This ammoniacal brine is pumped under pressure to a carbonating tower, which is about 70 feet high. The brine enters the tower about halfway up and flows down in a circuitous course, meeting carbon dioxide, which comes into the bottom of the tower under pressure. The carbon dioxide expands as it rises through the tower, and consequently produces a cooling effect. This and other cooling devices counterbalance the heat developed by the reaction, and establish the most desirable temperature (30° C. to 35° C.) for the absorption of the carbon dioxide by the ammoniacal brine.

The sodium bicarbonate, precipitated under the existing solubility conditions, is drawn off, filtered, and washed. The bicarbonate is then heated in iron pans:

$$\underset{\substack{\text{sodium}\\\text{bicarbonate}}}{2\,NaHCO_3} \longrightarrow \underset{\substack{\text{sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2}$$

The sodium carbonate thus obtained is nearly pure. Pure bicarbonate is obtained from it by passing carbon dioxide into a solution of the carbonate:

$$\underset{\substack{\text{sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2} \longrightarrow \underset{\substack{\text{sodium}\\\text{bicarbonate}}}{2\,NaHCO_3}$$

The process serves equally well for the production of potassium bicarbonate and of potassium carbonate.

495. Economy of the Solvay Process. — The carbon dioxide liberated in the conversion of the bicarbonate into the carbonate is used in the carbonating tower. Ammonium chloride is recovered from the water of the tower solution and heated with quicklime to regenerate the ammonia gas for another cycle of operations. Quicklime is obtained by heating limestone. During this process carbon dioxide is evolved and is used in the carbonating tower. Thus, after the process once starts, the principal cost of materials is for the water, salt, and limestone. Small quantities of an ammonium salt have to be purchased from time to time to replenish the slight, but unavoidable, loss of ammonia.

496. Sodium Hydroxide. — In order to meet the enormous demand for caustic soda (sodium hydroxide, NaOH) a number of processes for preparing it have been devised. The most efficient of these is the Castner process, which is based upon the following reaction for the electrolysis of brine:

$$\underset{\text{sodium chloride}}{2\,NaCl} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{chlorine}}{Cl_2} + \underset{\text{hydrogen}}{H_2}$$

The chief practical problem in the electrolysis of sodium chloride is to keep the chlorine from reacting with either the sodium hydroxide or the liberated hydrogen. The reaction with hydrogen would probably be explosive. In the Castner process, the electrolysis is carried on in a stone box, divided into three compartments (Fig. 177) by vertical partitions reaching nearly to the bottom. Brine is run into the two end compartments and pure water into the middle one. On the bottom of the tank is a thin layer of mercury, into

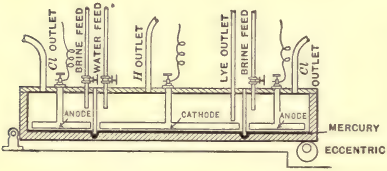


FIG. 177. — CASTNER CELL.

which the partitions dip, in order to prevent the mixing of the liquids in the end compartments with the liquid in the middle.

Several T-shaped anodes of Acheson graphite are suspended in each brine compartment. The layer of mercury is *negative* relative to the anode and *positive* relative to the cathode. The current, entering at the anode, passes through the brine to the mercury; the sodium moves with the current, while the chlorine is attracted to the anode:

$$\underset{\text{sodium chloride}}{NaCl} \longrightarrow \underset{\text{sodium}}{Na} + \underset{\text{chlorine}}{Cl}$$

The sodium is first liberated in contact with the mercury and amalgamates with it, the amalgam floating on the surface. An eccentric tilts the cell up and down at half-minute intervals. As the cell is inclined, the amalgam flows into the center compartment, which contains a weak solution of sodium hydroxide at the beginning of the process. The sodium continues to migrate with the current through the center compartment, leaves the mercury, and is finally liberated at the cathode. Here it reacts with water, forming sodium hydroxide:

$$\underset{\text{sodium}}{2\,Na} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{hydrogen}}{H_2}$$

As soon as the caustic soda solution has reached a specific gravity of 1.3, its concentration is kept constant by continuously drawing off a portion of the liquid and replacing it with a stream of fresh water. The solution is then evaporated in iron pots to drive off the water, and the caustic soda is either cast into sticks or run into iron drums.

The brine in the end compartments is kept circulating and salt is put in to keep its concentration constant.

The chlorine liberated at the anode is led off through pipes and is used in making bleaching powder. The hydrogen is usually a waste product. The mercury not only acts as a seal between the compartments, but it conducts the current from the end compartments to the middle.

By using a solution of potassium chloride instead of sodium chloride, the electrolytic process serves equally well for the manufacture of caustic potash, potassium hydroxide.

497. Hypochlorites. — Although chlorine is sold liquefied in steel cylinders, most of the chlorine for industrial uses is shipped in the form of hypochlorites. These powerful oxidizing and bleaching agents are salts of hypochlorous acid, $HClO$. There are several electrolytic processes for making hypochlorites.

When chlorine is passed into a cold solution of a caustic alkali, as sodium hydroxide, the following reaction occurs:

$$\underset{\substack{\text{sodium}\\ \text{hydroxide}}}{2\,\mathrm{NaOH}} + \underset{\text{chlorine}}{\mathrm{Cl_2}} \longrightarrow \underset{\substack{\text{sodium}\\ \text{hypochlorite}}}{\mathrm{NaClO}} + \underset{\substack{\text{sodium}\\ \text{chloride}}}{\mathrm{NaCl}} + \underset{\text{water}}{\mathrm{H_2O}}$$

Sodium hypochlorite is used in its water solution under the name of Javelle water.

Calcium hypochlorite is made in a similar manner by passing chlorine gas into milk of lime:

$$\underset{\substack{\text{calcium}\\ \text{hydroxide}}}{2\,\mathrm{Ca(OH)_2}} + \underset{\text{chlorine}}{2\,\mathrm{Cl_2}} \longrightarrow \underset{\substack{\text{calcium}\\ \text{hypochlorite}}}{\mathrm{Ca(ClO)_2}} + \underset{\substack{\text{calcium}\\ \text{chloride}}}{\mathrm{CaCl_2}} + \underset{\text{water}}{2\,\mathrm{H_2O}}$$

The conditions for the reaction are an excess of lime and a temperature below 33° C. The water solution of calcium hypochlorite made in this way is much used as a bleaching liquor. On account of its bulk it is not transported, but is made where it is to be used.

498. Bleaching Powder. — The compound containing available chlorine which can be profitably shipped is *bleaching powder*, a compound similar in composition to calcium hypochlorite. Chemists are not agreed as to the correct formula for bleaching powder, but it is often represented by $CaOCl_2$.

Bleaching powder is made by passing chlorine through a series of chambers containing slaked lime, spread in a thin layer on the floor or on shelves. The powder is shipped in tight containers, as moist air rapidly decomposes it. Bleaching powder yields chlorine when treated with dilute acids, even as weak as carbonic acid.

Upon the reaction with an acid depends the use of bleaching powder as a source of chlorine for bleaching cotton, linen, and other materials. Its use as a disinfectant, "chloride of lime," is due to the slow liberation of chlorine by moist air containing carbon dioxide. It is well to recall that both the bleaching and disinfecting action of chlorine depends in a large measure on the reaction:

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{hydrochloric acid}}{2\,HCl} + \underset{\text{nascent oxygen}}{O}$$

The active agent of bleaching powder is believed to be nascent oxygen.

499. Chlorates. — Potassium chlorate is made by the electrolysis of a warm concentrated solution of potassium chloride. The initial products of the electrolysis, namely, chlorine and potassium hydroxide, are brought together by stirring, and react, finally producing the chlorate:

$$\underset{\substack{\text{potassium}\\\text{hydroxide}}}{6\,KOH} + \underset{\text{chlorine}}{3\,Cl_2} \longrightarrow \underset{\substack{\text{potassium}\\\text{chlorate}}}{KClO_3} + \underset{\substack{\text{potassium}\\\text{chloride}}}{5\,KCl} + \underset{\text{water}}{3\,H_2O}$$

On cooling the solution, the potassium chlorate crystallizes out, and the remaining potassium chloride solution is again electrolyzed.

Potassium chlorate is the only chlorate of commercial importance. It is used in the manufacture of dyes and in making oxygen gas. The potash tablets used for sore throats are composed of this compound.

500. Hydrogen Peroxide. — This compound is prepared by the action of barium peroxide with a dilute acid (sulphuric or phosphoric). The barium peroxide is mixed with water to the consistency of cream. This mixture is then added to a dilute solution of phosphoric acid, care being taken to keep the temperature below 15° C. :

$$\underset{\text{barium peroxide}}{3\,BaO_2} + \underset{\text{phosphoric acid}}{2\,H_3PO_4} \longrightarrow \underset{\text{barium phosphate}}{Ba_3(PO_4)_2} + \underset{\text{hydrogen peroxide}}{3\,H_2O_2}$$

The precipitate of barium phosphate is allowed to settle and the solution of hydrogen peroxide drawn off.

The commercial form of hydrogen peroxide is its 3 % water solution. To prevent the peroxide from decomposition, the solution is kept slightly acid or a very small quantity of acetanilid is added. It is sold under various trade names, such as "Dioxogen" and "Aerozone."

Hydrogen peroxide is a clear, sirupy liquid about 1.5 times as dense as water. Concentrated hydrogen peroxide is likely to decompose with explosive violence. Even in the dilute 3 % water solution, the decomposition proceeds slowly according to the equation :

$$\underset{\text{hydrogen peroxide}}{H_2O_2} \rightleftarrows \underset{\text{water}}{H_2O} + \underset{\text{nascent oxygen}}{O}$$

Upon the activity of the nascent oxygen depend the uses of "peroxide" as a disinfecting and bleaching agent.

Harmful bacteria and decomposing organic matter are destroyed by it, hence its use as an antiseptic for superficial wounds and sores. It has very little action on living tissue, and the water formed in its decomposition does not give rise to further irritation, as do many other disinfectants. Silk, feathers, hair, and ivory are bleached by the oxidation of their coloring matters.

Some physicians object to the use of hydrogen peroxide for some purposes on account of the small amount of acid that it may contain. On this account, hydrogen peroxide should be mixed with limewater when used as a gargle.

501. Sodium Peroxide. — This compound is made by heating slices of sodium in air freed from carbon dioxide :

$$\underset{\text{sodium}}{2\,\mathrm{Na}} + \underset{\text{oxygen}}{\mathrm{O_2}} \longrightarrow \underset{\text{sodium peroxide}}{\mathrm{Na_2O_2}}$$

The temperature for the reaction must be kept between 300° C. and 400° C.

Sodium peroxide reacts violently with water, producing sodium hydroxide and oxygen :

$$\underset{\text{sodium peroxide}}{2\,\mathrm{Na_2O_2}} + \underset{\text{water}}{2\,\mathrm{H_2O}} \longrightarrow \underset{\text{sodium hydroxide}}{4\,\mathrm{NaOH}} + \underset{\text{oxygen}}{\mathrm{O_2}}$$

When the reaction is carefully regulated, it is a most convenient laboratory method for making small quantities of oxygen. Sodium peroxide should never be left on paper or other combustible material, as the heat of reaction with moisture may cause a blaze. Sodium peroxide is useful for making solutions of hydrogen peroxide for laboratory use, by sifting it into dilute acid solutions :

$$\underset{\text{sodium peroxide}}{\mathrm{Na_2O_2}} + \underset{\text{hydrochloric acid}}{2\,\mathrm{HCl}} \longrightarrow \underset{\text{hydrogen peroxide}}{\mathrm{H_2O_2}} + \underset{\text{sodium chloride}}{2\,\mathrm{NaCl}}$$

The use of sodium peroxide as an oxidizing and bleaching agent is increasing.

SOME IMPORTANT COMMERCIAL SALTS[1]

Scientific Name	Common Name	Formula	Important Uses
Ammonium sulphate	———	$(NH_4)_2SO_4$	Fertilizer; fireproofing fabrics
Aluminum sulphate	———	$Al_2(SO_4)_3$	Water purification
Calcium sulphate	Plaster of Paris	$2\,CaSO_4 \cdot H_2O$	Molds and casts
Ferrous sulphate	Green vitriol	$FeSO_4 \cdot 7\,H_2O$	Inks
Lead acetate	Sugar of lead	$Pb(C_2H_3O_2)_2$	Making pigments
Potassium cyanide	———	KCN	Extraction of gold
Potassium dichromate	———	$K_2Cr_2O_7$	Chrome tanning
Potassium ferrocyanide	Yellow prussiate of potash	$K_4Fe(CN)_6$	Making pigments, *e.g.* Prussian blue
Potassium permanganate	———	$KMnO_4$	Oxidizing agent; germicide
Sodium bicarbonate	Baking soda	$NaHCO_3$	Constituent of baking powders
Sodium silicate	Water glass	Na_2SiO_3	Protective coatings; calico printing; special cements
Sodium tetraborate	Borax	$Na_2B_4O_7 \cdot 10\,H_2O$	Soldering; soaps
Sodium thiosulphate	Hypo	$Na_2S_2O_3 \cdot 5\,H_2O$	Photography
Tin chloride	Tin salt	$SnCl_2 \cdot 2\,H_2O$	Dyeing; weighting silk

---

[1] Other common salts will be found in the table on page 41.

SUMMARY

Grades of Commercial Chemicals are crude, technical, C. P., and analyzed.

Hydrochloric Acid is made by heating salt with concentrated sulphuric acid. Hydrochloric acid is an active acid, yielding hydrogen and a chloride with most metals, except the noble metals and those with insoluble chlorides. It has a wide range of industrial uses.

Nitric Acid is made by heating sodium nitrate with sulphuric acid. Nitric acid reacts with most metals, forming nitrates and a gaseous product, which is almost invariably a reduction product, *e.g.*, nitric oxide or nitric peroxide. This is due to the readiness of nitric acid to give up oxygen. Easily oxidizable materials are attacked vigorously by nitric acid. Nitric acid is used in the manufacture of nitroglycerine, nitrocellulose products, and dyestuffs. Its salts have many important applications.

Sulphuric Acid is made by both the contact and the chamber processes. These are alike in that sulphur dioxide is first formed and then oxidized to sulphur trioxide, which is taken up by water. Sulphuric acid is a heavy, oily liquid, but is not so active as hydrochloric or nitric acid. The dilute acid yields hydrogen and a sulphate with the metals iron and zinc. The hot concentrated acid, with the metals copper and mercury, gives sulphur dioxide as a gaseous product, on account of the oxidizing action of the excess of sulphuric acid. Another important action of sulphuric acid is its dehydrating power, as many uses are based upon it. There is hardly an important industry which does not depend directly or indirectly on some use of this acid.

Sulphur is obtained from Louisiana, Sicily, Hawaii, and Japan. The commercial forms are flowers of sulphur and brimstone.

Ammonia is a by-product obtained in the destructive distillation of soft coal. Ammonia in water solution gives a cheap and very useful base. Liquid ammonia is used in ice-making and in refrigerating plants.

Sodium and Potassium Carbonates are made by the Solvay process, one of the first chemical processes to become highly efficient.

Sodium and Potassium Hydroxides are made by the Castner process, in which a solution of brine is electrolyzed.

Bleaching Powder is made by the reaction of chlorine with lime, and is used for bleaching and disinfecting.

Potassium Chlorate is made by the electrolysis of a solution of potassium chloride.

Hydrogen Peroxide is made by the reaction of a dilute acid with barium peroxide. The commercial article is a 3% water solution used for bleaching and disinfecting.

EXERCISES

1. Why do chemists prefer analyzed chemicals to the C. P. grade for their analytical operations?

2. Show how the solubility of hydrogen chloride is utilized in the manufacture of hydrochloric acid.

3. Why does a bottle of concentrated hydrochloric acid fume when opened to the air?

4. Why is hydrochloric acid inactive with lead and silver? How does it act with zinc and iron?

5. Write the equation for the reaction of hydrochloric acid with a carbonate. With a sulphide.

6. Why is concentrated sulphuric acid used in preparing both hydrochloric and nitric acids?

7. Why should not bottles of nitric acid be stored on wooden shelves?

8. Name three chemicals that should not be placed near concentrated nitric acid in a chemical stock room.

9. How could you determine whether a ring were brass or gold?

10. Explain why we do not get hydrogen as the gaseous product when copper reacts with concentrated nitric acid.

11. Why will a gas flame burn in the hot vapor of nitric acid?

12. Give the modern chemical name for each of the following acids: muriatic acid, oil of vitriol, and *aqua fortis.*

13. What difficulties arose in the commercial preparation of sulphur trioxide?

14. What grade of acid is best made by the contact process? By the chamber process?

15. Which contains less water, concentrated hydrochloric acid or concentrated sulphuric acid? Explain.

16. Account for the production of sulphur dioxide when sulphuric acid reacts with certain metals.

17. Write an equation for a laboratory preparation of hydrogen when sulphuric acid is used.

18. Why is concentrated sulphuric acid used in making nitroglycerine?

19. Of what advantage is the low melting point of sulphur in the Louisiana method of extraction?

20. What stimulus led to the development of electrical methods for manufacturing ammonia and nitrates?

21. Why was the price of soda lowered when the Solvay process was established?

22. Why is electrolytic caustic soda comparatively pure and cheap?

23. Why can chloride of lime be used as a disinfectant?

24. Why is bleaching powder priced according to the available amount of chlorine that it contains?

25. How is hydrogen peroxide serviceable to dentists?

26. Why is the household ammonia of bargain sales not necessarily cheap?

CHAPTER XLV

AGRICULTURE

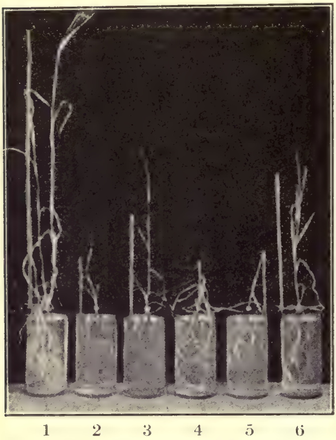
502. Fertility of the Soil. — In the United States, it has been customary to farm for the profit of the present generation, with little thought of those who were to follow. When the fertility of a farm became so low that agriculture was no longer profitable, the farm was frequently abandoned and those who wished to engage in agriculture sought virgin soil in other parts of the country. The result, as seen to-day, is that there are in the East hundreds of abandoned farms, and many soils of the Middle West, once considered inexhaustible, have greatly decreased in fertility.

At present, our more intelligent citizens are beginning to realize that little virgin soil exists in the United States, and that food must be furnished for a rapidly increasing population. The increased cost of living is causing much serious thought concerning the supply and demand of food. The restoration of fertility to worn-out farms is a problem that, sooner or later, must be solved if the country is to prosper. A fertile soil is necessary not only to the production of food for this growing nation, but for the production of over four fifths of all of the raw material used in our manufactures as well.

503. Elements Essential to Plant Life. — Let us consider some of the fundamental principles involved in the problem of increasing the fertility of farm lands. The elements hydrogen, carbon, oxygen, nitrogen, phosphorus, potassium, sulphur, magnesium, calcium, and iron are absolutely essential to plant life. If any one of them is lacking, no plant life can exist. In addition to these elements, silicon, chlorine, and sodium are necessary to the full development of many plants.

FIG. 178.—STAPLE CROPS: CORN.

Of the ten essential elements, carbon is derived from the carbon dioxide of the air; oxygen from air and water; hydrogen is derived from water. In few instances can nitrogen be taken from the air — never directly by flowering plants. This leaves six elements which farm crops always take from the soil. Nitrogen, phosphorus, and potassium frequently become diminished to such an extent that the soil fails to yield a profitable crop. For this reason nitrogen, phosphorus, and potassium compounds constitute the essential ingredients of commercial fertilizers. In addition to such compounds, it becomes necessary in some instances to add compounds containing calcium, magnesium, and sulphur. Elements taken from the soil in large quantities by crops must be returned to it in the form of suitable compounds, if the soil is not to decrease in fertility. Man cannot hope to have something made from nothing.



Copyright by *The Scientific American.*

FIG. 179. — WATER CULTURES OF BARLEY.

In the illustration (Fig. 179) is shown the effect of various elements on the growth of barley in water, viz.: (1) Complete manure; (2) No nitrogen; (3) No phosphoric acid; (4) No potash; (5) No lime; (6) No magnesia.

504. Soils. — Before the application of commercial fertilizers to the soil can be made intelligently, the composition of the soil must be studied. Soils are formed by the disintegration of rocks and by the accumulation of decayed organic matter. They may be deposited over, or near, the rocks from which they are derived, or may be transported many miles from the place of their origin. To-day water is the great transporting agent, but in the past enormous masses of rock and earth were brought from Canada by glaciers and deposited over the northern portion of the United States. A study of the native rock near a field will sometimes aid in determining the elements likely to be lacking in the soil.

The disintegration of feldspathic rocks results in the formation of clay soils. As the most common variety of feldspar is a silicate of potassium and aluminum, such a soil is not likely to be deficient in potassium. On the other hand, the disintegration of limestone yields a soil very likely to be deficient in that element. On account of the large number of fossils frequently found in limestone, a soil derived from it may be rich in phosphorus compounds. Loam is a mixture of sand with vegetable matter and frequently clay. Sandy soils are made up largely of particles of silica. They have a coarser structure than clay or lime soils, are "warmer" and more readily aerated, but less retentive of nitrogen and potassium compounds. Rains soon carry such compounds beyond the reach of plant roots, but a considerable portion of the material thus removed is returned to the plant by the capillarity of the soil.

The ground waters of clay soils carry in suspension minute particles of clay. On the evaporation of the water, these particles are deposited in a hard mass which forms an impervious layer on the surface of the soil. While the normal capillarity of a soil containing a large proportion of clay exceeds that of a sandy soil, the order may be reversed in dry weather on account of the "baking" of the surface of the clay soil.

The composition of the soil can be determined by the analysis of carefully selected samples, but this is work for a trained chemist and not for the student of elementary chemistry. The latter may, however, be able to determine, by the experimental application of fertilizers and by the growth of plants in a systematic manner, the elements in which a soil is deficient.

FIG. 180. — STAPLE CROPS: OATS.

505. Reserve Material. — There may be present in a soil a supply of all the elements necessary to plant life and yet the soil may be unproductive because the elements are contained in compounds which plants are unable to decompose readily. These combined elements, not directly available for plant food, constitute the reserve material of the soil. This reserve material is slowly converted into available compounds by the action of the atmosphere, organic matter, and certain inorganic substances.

506. Amendments. — A substance added to the soil, not because of the plant food it contains, but on account of the power it has to aid in the liberation of plant food from compounds containing it in unavailable forms, is called an *amendment*. Amendments convert the unavailable plant food into forms that can be assimilated by plants. Lime and ground gypsum are the amendments most frequently employed. Stable manure is sometimes of as much value as an amendment as for the plant food it contains.

SOURCES OF NITROGEN

The chief materials used for increasing the combined nitrogen of the soil are sodium nitrate, ammonium sulphate, calcium cyanamid, and various organic substances such as ground dried fish scrap, stable manure, guano, dried blood, cottonseed meal, and ground leather, hoofs, horns, and hair.

507. Sodium Nitrate, or Chili saltpeter, is obtained from extensive deposits along the western coast of South America. It is soluble in water, and the nitrogen it contains is readily assimilated by plants; 6 pounds of pure sodium nitrate contain about 1 pound of nitrogen. The commercial article seldom contains more than 95 % of that amount.

508. Ammonium Sulphate is a by-product of the coal gas works. It contains nitrogen in a form slightly less available for plant food than sodium nitrate; 4.7 pounds of pure ammonium sulphate contain 1 pound of nitrogen.

509. Calcium Cyanamid, "Cyanamid," or "lime-nitrogen," is of more than ordinary interest, as the method by which it is made illustrates one of the modern methods employed for the fixation of nitrogen, that is, for the conversion of the free nitrogen of the air into useful compounds. The reaction employed in the manufacture of "Cyanamid" was discovered in 1895. Calcium carbide, extensively employed in the manufacture of acetylene gas, is made by heating, in an electric furnace, a mixture of calcium oxide and coke to a temperature of about 3500° C.

$$\underset{\substack{\text{calcium}\\\text{oxide}}}{\mathrm{CaO}} + \underset{\text{carbon}}{3\,\mathrm{C}} \longrightarrow \underset{\substack{\text{calcium}\\\text{carbide}}}{\mathrm{CaC_2}} + \underset{\substack{\text{carbon}\\\text{monoxide}}}{\mathrm{CO}}$$

The calcium carbide thus prepared is cooled, crushed, heated to redness, and brought in contact with nitrogen, obtained from air. An impure calcium cyanamid results:

$$\underset{\substack{\text{calcium}\\\text{carbide}}}{\mathrm{CaC_2}} + \underset{\text{nitrogen}}{\mathrm{N_2}} \longrightarrow \underset{\substack{\text{calcium}\\\text{cyanamid}}}{\mathrm{CN\,.\,NCa}} + \underset{\text{carbon}}{\mathrm{C}}$$

The product thus obtained is further treated to remove carbides, phosphides, and sulphides, which, when brought in contact with the soil, would produce gases injurious to plant life.

The use of "Cyanamid" as a trade name is unfortunate, as the term really belongs to the chemical compound $\mathrm{CN\,.\,NH_2}$ of which calcium cyanamid, $\mathrm{CN\,.\,NCa}$, may be considered a salt.

Commercial "Cyanamid" varies in composition, but is made up chiefly of calcium cyanamid mixed with various substances such as calcium hydroxide, carbon, calcium nitrate, etc. The manufacturers state that it contains from 18½ % to 20 % of ammonia, by which they mean that it contains nitrogen sufficient to yield from 18½ % to 20 % of ammonia.

The nitrogen of "Cyanamid" is not directly available for plant food, but when the "Cyanamid" is mixed with the soil, changes take place by which the combined nitrogen is converted into substances, chiefly ammonium compounds, which can be assimilated by plants.

When calcium cyanamid is treated with hot water, ammonia gas is produced:

$$\underset{\substack{\text{calcium}\\\text{cyanamid}}}{CN.NCa} + \underset{\text{water}}{3\,H_2O} \longrightarrow \underset{\text{ammonia}}{2\,NH_3} + \underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3}$$

The ammonia may be passed into sulphuric acid to form ammonium sulphate, a valuable fertilizer (§ 508):

$$\underset{\text{ammonia}}{2\,NH_3} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{ammonium}\\\text{sulphate}}}{(NH_4)_2SO_4}$$

510. Fish Scrap. — Many thousands of tons of menhaden or porgy are caught each year on account of the oil they contain. After the oil has been extracted, the scrap is either dried, or partially dried, treated with sulphuric acid, and sold to manufacturers of fertilizers; the former by the name of "dry fish scrap" and the latter under the name of "wet acid scrap." "Dry fish scrap" contains about 9 % of available nitrogen. The "wet acid scrap" contains considerably less.

511. Guano consists of the excrement of birds, together with the remains of the birds themselves and portions of the fish on which they feed. Extensive deposits of guano exist on the islands along the coast of Peru. Peruvian guano was introduced into England as early as 1806, and was used in this country not later than 1832. It has been estimated that 18,500,000 tons of guano were used in 40 years. Deposits 30 feet thick are said to still remain untouched. A good grade of Peruvian guano contains about 14 % of combined nitrogen.

FIG. 181. — STAPLE CROPS: BEANS.

512. Minor Sources of Nitrogen. — Dried blood, cottonseed meal, hoofs, horn, leather, and hair are of minor importance as sources of nitrogen for plant food. Leather and hair are subjected to the fumes of hydrofluoric acid in order to render available the nitrogen they contain.

513. Fixation of Nitrogen. — One method for the conversion of the free nitrogen of the air into compounds for use as plant food has already been mentioned in describing the manufacture of "Cyanamid." The problem of burning the nitrogen of the air, thus causing it to combine directly with the oxygen, has received the attention of several brilliant chemists. The actual carrying out of the process is one of great difficulty, because the kindling point of nitrogen is above the temperature produced by the burning, and the temperature at which oxygen and nitrogen combine is very near the temperature at which the resulting compounds break down into their elements.

Several companies have been formed to produce nitric acid and nitrates by the use of electrical energy to cause the oxygen and nitrogen of the air to combine, thus forming oxides which can be absorbed by water or by bases to yield the desired compounds. The following equations may give the student some idea of the changes that take place :

$$\underset{\text{nitrogen}}{N_2} + \underset{\text{oxygen}}{2\,O_2} \longrightarrow \underset{\substack{\text{nitrogen}\\\text{peroxide}}}{2\,NO_2}$$

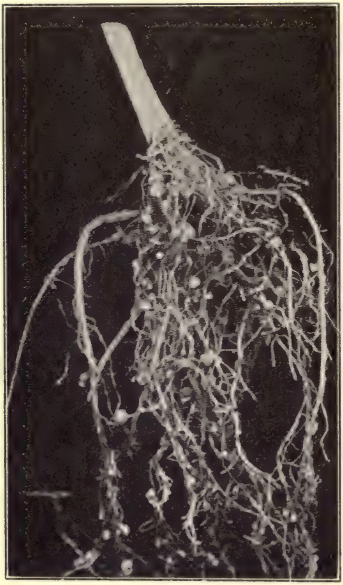
$$\underset{\substack{\text{nitrogen}\\\text{peroxide}}}{2\,NO_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\substack{\text{nitrous}\\\text{acid}}}{HNO_2} + \underset{\substack{\text{nitric}\\\text{acid}}}{HNO_3}$$

$$\underset{\substack{\text{nitrous}\\\text{acid}}}{2\,HNO_2} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\substack{\text{nitric}\\\text{acid}}}{2\,HNO_3}$$

$$\underset{\substack{\text{nitric}\\\text{acid}}}{2\,HNO_3} + \underset{\substack{\text{calcium}\\\text{hydroxide}}}{Ca(OH)_2} \longrightarrow \underset{\text{water}}{2\,H_2O} + \underset{\substack{\text{calcium}\\\text{nitrate}}}{Ca(NO_3)_2}$$

Some of the companies are at present meeting with success and bid fair to become important factors in the production of fixed nitrogen.

514. Nitrogen-fixing Bacteria. — While flowering plants do not possess the power to absorb directly from the air the nitrogen needed to build up their tissues, some of them are able to derive their nitrogen from parasitic plants which grow on their roots. These nitrogen-fixing bacteria are able to take nitrogen directly from the air which is mixed with the soil in which they grow. Leguminous plants, such as clover, beans, and peas, frequently obtain much of their nitrogen from the nitrogen-fixing bacteria growing on their roots. The infected roots have wartlike growths or nodules on them, caused by colonies of bacteria (Fig. 182). The earth around the nodule-bearing roots contains millions of germs ready to attack the roots of similar plants not infected. Such soil can be used to inoculate a soil lacking in the desired germs. The bacteria draw nourishment from the plants on whose roots they grow, but do much more good than harm. When a plant, for example clover, which has obtained its nitrogen from the air by the assistance of nitrogen-fixing bacteria, is plowed under, the soil is enriched in organic matter containing nitrogen which is rapidly rendered available. Cultures of nitrogen-fixing bacteria, for example, "Farmogerm" and "Ferguson's Composite Culture of Nitrogen-fixing Bacteria," are at present on the market and can be used to inoculate the seed of leguminous plants.



Copyright by *The Scientific American.*

FIG. 182. — BEAN ROOTS SHOWING NODULES.

Nitrogen-fixing bacteria will not thrive in an acid soil. It is, therefore, useless to inoculate a sour soil with them. The acids in the soil must be neutralized by the application of some alkali; in other words, the soil must be "sweetened." Finely ground limestone is probably the best substance to use for this purpose.

515. Nitrification. — The breaking down of organic compounds containing unavailable nitrogen into compounds containing available nitrogen is called *nitrification.* Such chemical changes are brought about by low forms of life, the nitrifying bacteria.

Substances such as stable manure, dried blood, dried fish scrap, and cotton-seed meal contain nitrogen compounds readily attacked by the nitrifying bacteria, which are always present in air and in soils. Three sets of bacteria take part in the process of nitrification : one set converts the organic nitrogen into ammonia, a second set changes the ammonia into nitrites, and the third set converts the nitrites into nitrates. The ammonia formed may escape into the air and much valuable fertilizing material may thus be lost. When the odor of ammonia is noticed around a stable or a manure pile, the farmer should realize that a valuable nitrogen compound is passing beyond his control, and he should apply some absorptive material such as earth or ground gypsum. Ammonia produced in the soil is not lost, because it is rapidly changed, by the action of the nitrifying bacteria, into nitrous acid and nitrites.

516. The Choice of Nitrogen Fertilizers. — The soluble nitrogen compounds, such as sodium nitrate and ammonium sulphate, contain nitrogen in a directly available form. They are readily soluble and are rapidly leached from the soil. These compounds should, therefore, be applied shortly before they are needed by the crop. They are of especial value for use in intensive farming. "Cyanamid," which will undoubtedly become a valued source of fixed nitrogen, is not readily soluble in water, and therefore is less likely to be leached from the soil than nitrates.

Where legumes are to be raised for the market, or where it is profitable to produce a crop of them to be plowed under, the nitrogen-fixing bacteria furnish a valuable means of supplying nitrogen to the soil. Guano, dried fish scrap, cottonseed meal, and dried blood are too limited in quantity and distribution, and are usually too expensive, for general use as fertilizers. Leather scrap, dried garbage, and peat are used to improve the mechanical condition of a fertilizer for use in seed drills rather than on account of the plant food they contain.

FIG. 183. — A FIELD OF CLOVER.

SOURCES OF PHOSPHORUS

The rock phosphates, phosphatic slag from iron and steel furnaces, bone, the Peruvian and Caribbean guanos, and mineral phosphate are important sources of phosphorus.

517. Rock Phosphates is a term applied to deposits directly traceable to an organic origin; they contain calcium phosphate which has been derived from the bones of animals.

Large deposits of rock phosphates occur in the United States. The deposits found in Florida, Tennessee, and South Carolina have been extensively worked, while those of Utah, Idaho, and Wyoming have not yet been developed.

518. Phosphatic Slag. — When an iron ore contains combined phosphorus, it is necessary to separate the phosphorus from the iron during the process of smelting and refining, as phosphorus renders iron and steel weak at ordinary temperatures. This separation is accomplished by lining the furnace with the oxides of calcium and magnesium and adding these substances to the furnace charge. The slag produced is of great value as a source of phosphorus for crops. It is now believed that the phosphorus exists in the slag as a double salt, calcium phosphate and calcium silicate, and as iron phosphate.

519. Bone. — The mineral ingredients of bone consist almost entirely of calcium phosphate and calcium carbonate. Bones have long been used as a source of phosphorus for farm crops.

520. Guano. — Peruvian guanos contain about 4.4 % of combined phosphorus (10 % P_2O_5). The Caribbean guanos contain, on the average, more than double that amount, although they are very poor in nitrogen.

521. Apatite is a mineral consisting of calcium phosphate in combination with calcium chloride and calcium fluoride. It furnishes the only common illustration of a mineral phosphate, that is, a substance containing phosphorus whose origin cannot be traced directly to an organic source. Large quantities of apatite were formerly imported from Canada for use in the manufacture of commercial fertilizers.

The expense of mining apatite does not permit it to enter into general competition with the rock phosphates.

FIG. 184. — STAPLE CROPS: HAY.

522. The Calcium Phosphates. — Calcium has a valence of 2 and phosphoric acid (H_3PO_4) is tribasic. The formula for normal calcium phosphate is, therefore, $Ca_3(PO_4)_2$. This is variously known as tricalcium phosphate, rock phosphate, and bone phosphate. Two calcium acid phosphates are known: dicalcium phosphate, $Ca_2H_2(PO_4)_2$, and monocalcium phosphate or "superphosphate of lime," $CaH_2(PO_4)_2$.

Dicalcium phosphate goes in trade by the name of "reverted phosphoric acid." It may be formed by a reaction between monocalcium phosphate and tricalcium phosphate:

$$\underset{\text{monocalcium phosphate}}{CaH_4(PO_4)_2} + \underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} \longrightarrow \underset{\text{dicalcium phosphate}}{2\,Ca_2H_2(PO_4)_2}$$

or by a reaction between calcium phosphate and sulphuric acid:

$$\underset{\substack{\text{tricalcium}\\ \text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{calcium}\\ \text{sulphate}}}{CaSO_4} + \underset{\substack{\text{dicalcium}\\ \text{phosphate}}}{Ca_2H_2(PO_4)_2}$$

The molecule of dicalcium phosphate, $Ca_2H_2(PO_4)_2 . 4\,H_2O$, contains 4 molecules of water of crystallization.

Dicalcium phosphate is not soluble in water, but is readily soluble in neutral ammonium citrate, and is soluble in juices secreted by plant roots. It makes up the so-called "citrate soluble phosphoric acid" of commercial fertilizers.

Monocalcium phosphate, when it occurs in fertilizers, is termed "soluble phosphoric acid" because it is readily soluble in water and directly absorbed by plants. It is prepared by the action of sulphuric acid on tricalcium phosphate. The final equation representing the reaction is commonly written:

$$\underset{\substack{\text{tricalcium}\\ \text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{2\,H_2SO_4} \longrightarrow \underset{\substack{\text{calcium}\\ \text{sulphate}}}{2\,CaSO_4} + \underset{\substack{\text{monocalcium}\\ \text{phosphate}}}{CaH_4(PO_4)_2}$$

This equation does not take into account the water of crystallization of either the monocalcium phosphate ($CaH_4(PO_4)_2 . H_2O$) or that of the crystallized calcium sulphate ($CaSO_4 . 2\,H_2O$).

Monocalcium phosphate together with the dicalcium phosphate constitutes the *available phosphoric acid* of commercial fertilizers.

Tricalcium phosphate is insoluble in water and in neutral ammonium citrate. It constitutes the *unavailable phosphoric acid* of a fertilizer. In the soil it slowly becomes available, and gradually yields a supply of phosphorus to plants for several years. The sum of the mono-, di-, and tri-calcium phosphates is the *total phosphoric acid* of a fertilizer.

523. Sources of Potassium. — Potassium enters the virgin soil chiefly through the disintegration of clay-producing rocks, such as granite and syenite, both of which contain potassium feldspar.

Potassium chloride, derived from extensive deposits in Germany, is, at the present time, the principal potassium compound used as a fertilizer.

Potassium sulphate is also used in fertilizers, but is not so cheap a source of potassium as the chloride.

Kainite, $MgSO_4 . KCl . 3 H_2O$, a compound also imported from Germany, is another source of potassium for agricultural purposes. The formula for kainite shows that, in addition to potassium, it contains the elements magnesium and sulphur, which are essential to plant life.

Wood ashes contain soluble potassium compounds and would be of great value as a source of potassium for plant food if the supply were large.

Potassium feldspar, which occurs in this country in enormous quantities, contains from 12% to 17% of potash. Thus far no method economically profitable has been found for converting it into compounds containing potassium in a soluble form. While rocks containing potassium silicates are being weathered slowly, and the potassium which they contain is being made available, the process does not go on with sufficient rapidity to meet the demands of farm crops. On the

FIG. 185. — STAPLE CROPS: POTATOES.

other hand, the fact that the potassium is largely contained in insoluble silicates assures a large supply of reserve plant food. Economic necessity will eventually require the chemist to discover methods of making the potassium of feldspars available. At present, the solution of the problem does not seem to be far distant.

524. Term Used in Market Quotations. — The nitrogen content of a fertilizer may be guaranteed as "available nitrogen," as "ammonia," or as "units of ammonia." By "available nitrogen" is meant nitrogen contained in compounds which may be assimilated by plants. The "percentage of ammonia" does not mean that the fertilizer actually contains ammonia, but that it contains available nitrogen in a quantity equal to that in the per cent of ammonia named. By the term "unit of ammonia" is meant a quantity of available nitrogen equal to that contained in 1 % of ammonia. A few examples may make the meaning of these terms clear. A fertilizer is guaranteed to contain 2 % of ammonia. What is the least amount of available nitrogen it should contain?

Taking the atomic weight of nitrogen as 14.01[1] and that of hydrogen as 1.008, the molecular weight of ammonia may be readily calculated to be 17.034.

$$\begin{aligned} N &= 14.010 \\ H_3 &= \underline{\ \ 3.024} \\ &\ 17.034 \end{aligned}$$

Of these 17.034 parts, 14.01 are nitrogen. $14.01 \div 17.034 = .8225$, or a little over .8 of the 2 % of ammonia would be available nitrogen, or, more exactly, $.8225 \times 2\ \%$

---

[1] The *exact* atomic weights (International Committee standard) are used in the calculations for fertilizers. A small variation in the atomic weight might mean a difference in pounds when a calculation involves a ton of fertilizer.

or 1.645 %. In other words, each 100 pounds of the fertilizer should contain 1.645 pounds of available nitrogen; and a ton, or 2000 pounds, would contain 20 × 1.645 pounds or 32.9 pounds.

Now the nitrogen might be contained in the fertilizer in various compounds, for example, sodium nitrate, dried fish scrap, or tankage. How much sodium nitrate guaranteed to contain 95 % of $NaNO_3$ would be required to yield 32.9 pounds of nitrogen? This quantity can be found by the following calculation:

$$\begin{aligned} Na &= 23.00 \\ N &= 14.01 \\ O_3 &= \underline{48.00} \\ & 85.01 \end{aligned}$$

If 85.01 pounds of pure sodium nitrate would yield 14.01 pounds of nitrogen, 85.01 ÷ 14.01 or 6.07 pounds of sodium nitrate would yield 1 pound of nitrogen; 32.9 × 6.07, or 199.7 pounds of pure sodium nitrate would be required for one ton of the fertilizer guaranteed to contain 2 % of ammonia. But the commercial sodium nitrate was only 95 % pure. Therefore 199.7 pounds is only 95 % of the quantity of commercial sodium nitrate required. The actual amount required would be 199.7 ÷ .95 or 210.2 pounds. Thus we have calculated that 210.2 pounds of 95 % sodium nitrate would be required in each ton of a fertilizer to have it contain 2 % of nitrogen reckoned as ammonia, or 1.64 % of available nitrogen.

If, instead of using sodium nitrate to furnish the nitrogen for the 2 % ammonia fertilizers, a tankage containing 6 units, or 6 %, of ammonia were employed, the amount of tankage required per ton of fertilizer can be calculated as follows:

Two per cent of ammonia is 40 pounds per ton. One ton of the 6 % tankage in question would contain 120 pounds of nitrogen reckoned as ammonia; $\frac{40}{120}$ or $\frac{1}{3}$ of a ton of the tankage would be required per ton of the fertilizer. If the value of the fertilizer is indicated in terms of nitrogen, this value may be converted into terms of ammonia by multiplying the percentage of nitrogen by 1.2151 or $17.034 \div 14.01$.

The combined phosphorus in a fertilizer is generally guaranteed in terms of phosphoric acid, by which is meant not the compound H_3PO_4 but its anhydride P_2O_5. The terms "soluble," "available," and "total phosphoric acid" are often used in connection with the guarantee. The meaning of these has already been explained. The mono-, di-, and tri-calcium phosphate content is always reduced to terms of phosphoric anhydride. This may be readily accomplished by considering monocalcium phosphate to be $CaO \cdot 2\,H_2O \cdot P_2O_5$, dicalcium phosphate to be $2\,CaO \cdot H_2O \cdot P_2O_5$, tricalcium phosphate to be $3\,CaO \cdot P_2O_5$, and then making use of a method similar to that employed in the reduction of ammonia to terms of nitrogen. The phosphoric acid (P_2O_5) content of a fertilizer can also be readily converted into terms of rock phosphate (Ca_3PO_4).

The combined potassium contained in a fertilizer is usually reckoned in terms of "potash"; that is, the chemical compound having the formula K_2O. Potassium chloride may be considered as having been formed by a reaction between potash (K_2O) and hydrochloric acid (HCl):

$$\underset{\textbf{potash}}{K_2O} + \underset{\substack{\textbf{hydrochloric}\\\textbf{acid}}}{2\,HCl} \longrightarrow \underset{\textbf{water}}{H_2O} + \underset{\substack{\textbf{potassium}\\\textbf{chloride}}}{2\,KCl}$$

By use of this equation, the relation between the potash content of a fertilizer and potassium chloride may be readily calculated.

Numbers are often used to indicate the plant food contained in a fertilizer; for example, it is spoken of as a 4–8–2 or a 9–20 fertilizer. The first of these numbers relates to the percentage of nitrogen, the second to the percentage of "phosphoric acid" (P_2O_5), and the third to the percentage of "potash" (K_2O) contained in the fertilizer. A 4–8–2 fertilizer contains 4 % of nitrogen, 8 % of "phosphoric acid," and 2 % of "potash." A 9–20 fertilizing material contains 9 % of nitrogen and 20 % of "phosphoric acid." As may be seen from the above figures, a fertilizer always contains a large per cent of inert material.

525. Soil Stimulants. — Combined calcium is generally added to the soil in the form of air-slaked lime, made by exposing quicklime, CaO, to the atmosphere. Air-slaked lime consists of calcium hydroxide mixed with calcium carbonate. It is of value, not on account of the plant food it contains, but on account of its power to neutralize acids in the soil, and its power to convert unavailable substances into plant food. It should never be forgotten that the soil is not being made permanently richer by the addition of lime, but, on the contrary, its application aids in the more rapid exhaustion of the soil This has been recognized by the agriculturalists of Europe, and has given rise to such proverbs as "Lime makes a rich father and a poor son."

Slaked lime is caustic in its action, that is, it destroys organic matter. It, therefore, decreases the amount of organic matter in the soil. This is in most cases undesirable. The greater length of time lime remains exposed to the air, the greater the quantity of calcium carbonate it contains and the less caustic it becomes.

526. Limestone. — The addition of very finely ground limestone to the soil has in many cases proved valuable on account of its ability to neutralize undesirable acids in the soil. It often contains magnesium compounds and fossils which may yield calcium phosphate. Limestone is not caustic in its action and increases rather than diminishes the fertility of the land to which it is added. It is, therefore, preferable to lime.

527. Gypsum. — Ground gypsum, or "land plaster," aids in the liberation of plant food from insoluble compounds in the soil. It acts less rapidly than lime, and is not so valuable for neutralizing acids. On the other hand, it has comparatively little influence on the organic matter of the soil, and, in this respect, is superior to lime.

528. Farm Problems and Scientific Knowledge. — The time when the uneducated and untrained man can be a successful farmer is rapidly passing. A knowledge of the composition and nature of the soil to be tilled, and of the crops to be raised, is essential. The farmer should know whether his land needs a complete fertilizer, that is, one containing nitrogen, phosphoric acid, and potash, or a fertilizer containing only one or two of these substances. He should have information concerning the sources and prices of fertilizing materials and be able to calculate the substance which will furnish the most of the desired element or elements for the least money. He should understand that the amount of an

Fig. 186. — Staple Crops: Wheat.

element taken from the soil varies with the crop and should be able to plan a desirable rotation of crops. He should know when to use a large supply of available plant food, and when it will pay to use a fertilizer containing material that will slowly be converted into plant food. He should understand the value of fertilizing materials produced on the farm, and should know how to prevent the waste of any of them.

But these are only a few of the problems the farmer has to face. Equally important are the mechanical condition of the soil, the quality of the seed planted, and the kind of stock raised. He must understand the utility of farm implements, know the pests, both insect and parasitic, which attack his crops, and how to reduce their depredations to a minimum. In fact, each farmer has his own problems to solve ; problems whose solution requires as much scientific knowledge and business skill as any other industry demands.

CONSTITUENTS OF STAPLE CROPS

In the following table, the nitrogen, the phosphorus, and the potassium content of some staple crops is given in terms corresponding to the numbers used to indicate the plant food contained in a commercial fertilizer (§ 524, pp. 581–582).

Staple Crop	100 Pounds of Crop Contain			Illustration in Text
	Nitrogen	Phosphorus (P_2O_5)	Potassium (K_2O)	
Corn (seed) . . .	1.60 lb.	0.572 lb.	0.373 lb.	Fig. 178
Oats (seed) . . .	1.76 lb.	0.687 lb.	0.482 lb.	Fig. 180
Wheat (seed) . . .	2.08 lb.	0.758 lb.	0.518 lb.	Fig. 186
Potatoes (tubers) .	0.34 lb.	0.160 lb.	0.578 lb.	Fig. 185
Beans (seed) . . .	3.90 lb.	0.962 lb.	1.217 lb.	Fig. 181
Clover Hay (in bud)	2.45 lb.	0.710 lb.	2.591 lb.	Fig. 183
Hay (air dry) . . .	1.05 lb.	0.343 lb.	0.964 lb.	Fig. 184

SUMMARY

Elements Essential to Plant Life are calcium, carbon, hydrogen, iron, magnesium, nitrogen, oxygen, phosphorus, potassium, and sulphur. A soil is likely to become deficient in compounds of nitrogen, phosphorus, and potassium, and consequently become infertile.

A Complete Fertilizer contains compounds of nitrogen, phosphorus, and potassium in forms suitable for plant food.

Sources of Nitrogen valuable for use in fertilizers are sodium nitrate, ammonium sulphate, calcium cyanamid, and various organic substances such as guano, dried blood, and cottonseed meal.

Fixation of Nitrogen is the conversion of the free nitrogen of the air into useful compounds. This is brought about by chemical processes, and by the action of cultures of nitrogen-fixing bacteria.

Nitrification is the conversion, by processes of decay, of nitrogenous organic compounds into compounds that can be absorbed by the roots of plants. It is accomplished by bacteria.

The Chief Sources of Combined Phosphorus for use in fertilizers are the rock phosphates, mineral phosphates, bones, Peruvian guano, and phosphatic slag from iron blast furnaces.

Monocalcium Phosphate is soluble and directly available as plant food.

Dicalcium Phosphate, "reverted calcium phosphate," is not soluble in water, but can be dissolved by the root juices of plants, and for this reason is available.

Tricalcium Phosphate is not available for plant food until it has been converted into some soluble compound.

Sources of Combined Potassium for use in fertilizers are potassium chloride, potassium sulphate, kainite, and wood ashes.

EXERCISES

1. Why should the farmer be familiar with the "Law of Conservation of Matter" which states that matter is indestructible, and that something cannot be made from nothing?

2. Of the ten elements necessary to plant life, name three that are most likely to be lacking in a soil.

3. What is meant by the fixation of nitrogen?

4. Briefly describe two chemical processes for the fixation of nitrogen.

5. What are nitrogen-fixing bacteria, and under what conditions do they flourish?

6. Under what circumstances is it advantageous to make use of nitrogen-fixing bacteria?

7. Define nitrification and describe the steps in the process.

8. What is meant by the terms *soluble, reverted, insoluble,* and *available* when used in connection with the phosphoric acid of a fertilizer?

9. Mention important compounds of potassium used in fertilizers.

10. What is a complete fertilizer?

11. What is a 4–8–2 fertilizer?

12. A commercial lot of sodium nitrate is guaranteed to be 91% pure. What is the least quantity of available nitrogen that should be contained in one ton of the substance?

13. A sample of muriate of potash was reported by a competent analyst to contain 48% of potash. What per cent of potassium chloride did the sample contain?

14. A fertilizer is guaranteed to contain 2.43% of ammonia. This is equivalent to what per cent of nitrogen?

15. A sample of soluble bone phosphate was found to contain 14% of soluble phosphoric acid. How many pounds of monocalcium phosphate per ton would it contain?

16. A sample of tankage is guaranteed to contain 6 units of ammonia. What is the percentage content of nitrogen?

17. When nitrogen is worth 19 cents a pound, and phosphoric acid $3\frac{1}{2}$ cents a pound, what is the commercial value of a 9–20 (9 % ammonia–20 % bone phosphate) tankage?

18. Making use of the quotations given below, calculate
  (*a*) the quantities of nitrate of soda, dissolved S. C. rock, and muriate of potash;
  (*b*) the cost of each;
  (*c*) the number of pounds of inert matter required for one ton of a 3–9–7 fertilizer.

Market quotations:

Nitrate of soda, 15 % nitrogen	$ 57.00 per ton
Dissolved S. C. rock, 14 % available P_2O_5 .	12.60 per ton
Muriate of potash, 48 % K_2O	48.00 per ton

19. Sometimes experiment stations publish factors by the use of which the approximate "commercial valuation" of a fertilizer can be calculated. The "commercial valuation" is the retail cash price in dollars per ton of the unmixed constituents of the fertilizer. Such a table reads:

Multiply the percentage of nitrogen by	3.8
Multiply the percentage of available phosphoric acid by .	0.9
Multiply the percentage of insoluble phosphoric acid by .	0.4
Multiply the percentage of potash by	1.00

The factors of course vary with the price.

Making use of the factors given above calculate the commercial valuation of a fertilizer guaranteed to contain —

Nitrogen	1.31 %
Available phosphoric acid	9.87
Total phosphoric acid	11.34
Potash	5.41

The insoluble phosphoric acid equals the total phosphoric acid minus the available phosphoric acid.

CHAPTER XLVI

CHEMICAL CALCULATIONS

529. Molecular Weight. — The molecular weight of an element, or of a compound, may be readily calculated from its formula. For example, the formula for ordinary oxygen is O_2 and the atomic weight of oxygen is 16. The molecular weight of oxygen is, therefore, 2 × 16 or 32. *The molecular weight is always the sum of the atomic weights represented by the chemical formula.* The formula for sulphuric acid is H_2SO_4. Referring to the table of approximate atomic weights (page 600), the student will see that the atomic weight of hydrogen is given as 1, that of sulphur as 32, and that of oxygen as 16. The molecular weight of sulphuric acid is, therefore, 98.

$$\begin{array}{lll} H_2 = 2 \times 1 & = & 2 \\ S & = & 32 \\ O_4 = 4 \times 16 & = & \underline{64} \\ & & 98 \text{ Molecular weight of sulphuric acid.} \end{array}$$

530. Specific Gravity of a Gas is the weight of that gas compared with the weight of an equal volume of air measured under like conditions. A definite relation exists between the specific gravity of a gas and its molecular weight; the molecular weight of a gas is 28.9 times its specific gravity, or conversely, the specific gravity of gas is $\frac{10}{289}$ of its molecular weight. If we want to know whether a certain gas is heavier or lighter than air, we simply have to calculate its molecular weight and note whether it is more or less than 28.9. If it is more than

28.9, the gas is heavier than air ; if less, the gas is lighter than air.

531. Vapor Density is the weight of a given volume of a gas compared with the weight of an equal volume of hydrogen. In other words, it is the specific gravity of a gas when hydrogen is taken as the standard of comparison. The vapor density of a gas is one half of its molecular weight. The molecular weight of a gas is twice its vapor density.

532. Weight of a Liter of a Gas. — To calculate the weight of a liter of a gas, we may take the weight of a liter of hydrogen and multiply it by the vapor density of the gas. For example, to calculate the weight of a liter of carbon dioxide measured at standard conditions (0° C. and at a pressure equal to a column of mercury 760 mm. high) we proceed as shown below :

CO_2 is the formula for carbon dioxide.

$$\begin{array}{ll} C & = 12 \\ O_2 & = \underline{32} \\ & \quad 44 \text{ Molecular weight of carbon dioxide.} \\ 44 \div 2 & = 22 \text{ Vapor density of carbon dioxide.} \end{array}$$

0.09 gram is the weight of a liter of hydrogen.

$22 \times .09$ g. $= 1.98$ g. Weight of a liter of carbon dioxide.

533. Calculations from Chemical Equations may be conveniently divided into three classes, those involving weight only, those involving both weight and volume, and those involving volume only.

534. Problems involving Weight Only have to do with cases where from a given weight of one substance in a reaction the weight of some other substance in the reaction is to be calculated. For example, a person desires to calculate the number of pounds of hydrochloric acid gas that could be obtained from 500 pounds of pure sodium chloride.

He first writes the equation which represents the reaction which would take place:

$$\underset{\substack{\text{sodium}\\\text{chloride}}}{2\,NaCl} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{2\,HCl}$$

He may then state the problem by placing 500 pounds above the HCl and a question mark above the NaCl:

$$\overset{?\text{ lb.}}{2\,NaCl} + H_2SO_4 \longrightarrow Na_2SO_4 + \overset{500\text{ lb.}}{2\,HCl}$$

Now the same relation exists between actual weights as exists between the weights represented by the chemical equation. 2 HCl represents 2×36.5 or 73 parts by weight, and 2 NaCl represents 2×58.5 or 117 parts by weight. Therefore, $117 : 73 :: x \text{ lb.} : 500 \text{ lb.}$

$$x = 801 + \text{ pounds of sodium chloride.}$$

The solution of the problem may be briefly stated as follows:

$$\underset{117}{\overset{?\text{ lb.}}{2\,NaCl}} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{73}{\overset{500\text{ lb.}}{2\,HCl}}$$

$$\begin{array}{ll} \begin{array}{l} Na = 23 \\ Cl \;= \underline{35.5} \\ \quad\;\; 58.5 \times 2 = 117 \end{array} & \qquad\qquad \begin{array}{l} H = \;\;1 \\ Cl = \underline{35.5} \\ \quad\;\; 36.5 \times 2 = 73 \end{array} \end{array}$$

$$117 : 73 :: x \text{ lb.} : 500 \text{ lb.}$$

$$x = 801 + \text{ lb. of sodium chloride.}$$

535. Problems involving Both Weight and Volume include cases in which the object is to determine the weight of a certain compound required for the production of a given volume of a gas, or *vice versa*. The solution of this class of problems with the least amount of work possible requires a knowledge of the generalization that when weights are expressed in grams, every molecule of gas represented by the equation stands for 22.2 liters; when weights are expressed in kilograms every molecule of gas stands for 22.2 cubic meters; and when weights are expressed in ounces (avoirdupois) each molecule of gas stands for 22.2 cubic feet.

Suppose the problem to be: What weight of calcium carbide would be required for the production of 1000 cubic feet of acetylene? The chemical equation representing the reaction is

$$\underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\substack{\text{calcium}\\\text{hydroxide}}}{Ca(OH)_2} + \underset{\text{acetylene}}{C_2H_2}$$

Since the atomic weight of calcium is 40 and that of carbon 12, CaC_2 stands for 64 parts by weight. As the problem calls for cubic feet of acetylene, we would consider these parts by weight to be ounces. Now, remembering that when parts by weight are taken as ounces, each molecule weight of the gas stands for 22.2 cubic feet, we see that 64 ounces of calcium carbide would yield 22.2 cubic feet of acetylene. The calculation of the number of ounces of calcium carbide required to yield 1000 cubic feet of acetylene then becomes a simple matter. The problem and its solution may be represented as follows:

$$\underset{64\text{ oz.}}{\overset{x\text{ oz.}}{CaC_2}} + 2\,H_2O \longrightarrow Ca(OH)_2 + \underset{22.2\text{ cu. ft.}}{\overset{1000\text{ cu. ft.}}{C_2H_2}}$$

$$\begin{aligned} Ca &= 40 \\ C_2 = 2 \times 12 &= \underline{24} \\ &\ 64 \end{aligned}$$

$C_2H_2 = 1$ molecule of acetylene and in the problem stands for 22.2 cu. ft.

$$64 : 22.2 :: x : 1000$$

$$x = 288.2+ \text{ oz. or } 18.0+ \text{ lb.}$$

If two molecules of the gas mentioned in the problem are represented in the equation, the volume of the gas is

22.2 × 2 or 44.4 cubic feet, cubic meters, or liters, according to whether the parts by weight represent ounces, kilograms, or grams. For example, suppose the problem to be: How many liters of ammonia can be obtained by heating 20 grams of ammonium sulphate with sufficient slaked lime? The equation for the reaction and the solution of the problem may be represented as follows:

$$\underset{\text{132 g.}}{\overset{\text{20 g.}}{(NH_4)_2SO_4}} + Ca(OH)_2 \longrightarrow CaSO_4 + 2\,H_2O + \underset{2 \times 22.2}{\overset{x \text{ liters}}{2\,NH_3}}$$

or 44.4 liters
of ammonia.

$$\begin{array}{lll} N & = 14 & \\ H_4 & = \underline{\ 4} & \\ & 18 \times 2 = & 36 \\ S & = & 32 \\ O_4 & = & \underline{64} \\ & & 132 \end{array}$$

$$132 : 44.4 :: 20 : x$$

$$x = 6.7 + \text{ liters.}$$

536. Problems involving volume only are simple to solve, because the same relation exists between the volumes of gases that exists between the numbers of molecules of the same gases represented in the chemical equation. Suppose that we wish to calculate the number of liters of oxygen required for the complete combustion of 250 liters of acetylene. The equation which represents the reaction is:

$$\underset{\textbf{acetylene}}{2\,C_2H_2} + \underset{\textbf{oxygen}}{5\,O_2} \longrightarrow \underset{\substack{\textbf{carbon}\\ \textbf{dioxide}}}{4\,CO_2} + \underset{\textbf{water}}{2\,H_2O}$$

This shows that 2 molecules of acetylene require for complete combustion 5 molecules of oxygen, and consequently 2 volumes of acetylene require 5 volumes of oxygen. The problem and its solution may therefore be stated as follows:

$$\begin{array}{l} 250\text{ l.}\quad x\text{ l.} \\ 2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O \\ 2\text{ l.}\qquad 5\text{ l.} \\ 2\text{ l.} : 5\text{ l.} :: 250\text{ l.} : x\text{ l.} \\ \qquad x = 625\text{ l. of oxygen.} \end{array}$$

537. Preparation of a Solution of Desired Specific Gravity. — It frequently becomes necessary to prepare a solution of some desired specific gravity from one of the more concentrated solutions purchased from dealers in chemicals. For instance, one may wish to prepare a solution of sulphuric acid having a specific gravity of 1.20 by the addition of water to the commercial acid having a specific gravity of 1.84. How many cubic centimeters of acid and how many of water would be required to make 1000 cubic centimeters of the solution having a specific gravity of 1.2?

A formula for the solution of such problems may be derived as follows:

Let x = number of cubic centimeters of heavier liquid.
Let y = number of cubic centimeters of lighter liquid.
Let M = specific gravity of the desired mixture.
Let H = specific gravity of the heavier liquid.
Let L = specific gravity of the lighter liquid.
Let V = volume of the mixture.

We would then have

(1) $x + y = V$ and

(2) $Hx + Ly = VM.$

Multiplying (1) by L we obtain

(3) $Lx + Ly = LV.$

Subtracting (3) from (2) we get

(4) $Hx - Lx = VM - LV$ or $x(H - L) = V(M - L).$

Therefore

$$x = \frac{M - L}{H - L} V. \tag{5}$$

Having derived the formula just given, the solution of the problem given above becomes merely a matter of substituting for H, L, M, and V the values assigned to them and then solving for x. In the problem

$H = 1.84$
$L = 1.00$
$M = 1.20$ and
$V = 1000$ cubic centimeters.

Making the proper substitutions in the formula we obtain

$$x = \frac{1.20 - 1.00}{1.84 - 1.00} \times 1000 \text{ or } \frac{20}{84} \times 1000 \text{ or } 238.1 \text{ c.c.}$$

Therefore, 238.1 cubic centimeters of sulphuric acid having a specific gravity of 1.84 should be added to 761.9 cubic centimeters of water in order to obtain 1000 cubic centimeters of a dilute acid having a specific gravity of 1.2.

The formula given does not take into account any change in volume which may occur on mixing the liquids used, but it is sufficiently accurate for use in most of the cases that will arise during laboratory work in an elementary course in chemistry.

538. Normal Solutions. — A normal solution is a solution a liter of which contains either 1 gram of replaceable hydrogen, or a weight of an element, or of a radical, that is equal in combining power to 1 gram of hydrogen.

A normal solution of an acid contains 1 gram of replaceable hydrogen per liter. To calculate the number of grams of acid per liter contained in a normal solution of an acid, divide the molecular weight of the acid by the number of replaceable hydrogen atoms which the molecule contains.

A normal solution of a base contains 17 grams of hydroxyl (OH) per liter. To calculate the number of grams of a base contained in 1 liter of its normal solution, divide the molecular weight of the base by the number of OH groups it contains.

539. Problems involving Normal Solutions. — When neutralization takes place, each acid hydrogen atom has united with a hydroxyl radical and *vice versa*, or, in other words, a given weight of hydrogen $(H=1)$ has entered into chemical combination with 17 times $(OH=17)$ its weight of hydroxyl. It therefore follows that a given volume of a normal solution of any acid will neutralize an equal volume of a normal solution of any base.

The fact just mentioned is of great service in making calculations connected with *titration* work; that is, with the determination of the unknown concentration of a solution by making use of a solution of known concentration. Suppose that a chemist finds that 15 cubic centimeters of a fifth-normal (N/5) solution of hydrochloric acid exactly neutralizes 30 cubic centimeters of a solution of sodium hydroxide of unknown concentration, and he desires to calculate the number of grams of sodium hydroxide per liter that its solution contains. If the solution of sodium hydroxide had been fifth-normal, 30 cubic centimeters of fifth-normal hydrochloric acid would have been required to neutralize 30 cubic centimeters of the base. But it only required 15 cubic centimeters of the fifth-normal acid to neutralize 30 cubic centimeters of the base. The solution of the base was therefore $\frac{15}{30}$ of fifth-normal or half as concentrated as the acid. Now a normal solution of sodium hydroxide contains 40 grams of sodium hydroxide per liter $\left[\begin{array}{l} \mathrm{Na} = 23 \\ \mathrm{OH} = \underline{17} \\ \qquad\ \ 40 \end{array}\right]$. A fifth-normal solution of sodium hydroxide would contain $\frac{40}{5}$ or 8 grams of sodium hydroxide per liter, and the solution in question would contain $\frac{15}{30}$ of 8 grams or 4 grams of sodium hydroxide per liter.

SUMMARY

Specific Gravity is the weight of a substance compared with the weight of an equal volume of a substance taken as a standard. The weight of the standard is considered to be 1. Water is the standard for liquids and solids. Air is usually considered as the standard for gases.

Vapor Density is a term used in place of specific gravity when hydrogen is the standard. The vapor density of a gas is the number of times that gas is as heavy as an equal volume of hydrogen, measured under like conditions. The vapor density of a gas is equal to one half its molecular weight.

The Weight of a Liter of a Gas equals the weight of a liter of hydrogen multiplied by the vapor density of the gas (0.09 g. × v. d.).

In Solving Problems Involving Weight Only, the student should remember that actual weights are proportional to the weights represented by the chemical equation involved.

For the Solution of Problems Involving Weight and Volume, it is convenient to make use of the generalization that, when weights are expressed in grams, each molecule of gas represented in the chemical equation stands for 22.2 liters.

During the Solution of Problems Involving Volume Only, the student should bear in mind the fact that the same relation exists between volumes that exists between the numbers of molecules of gases represented by the equation.

A Normal Solution of an Acid contains 1 gram of replaceable hydrogen per liter.

A Normal Solution of a Base contains 17 grams of hydroxyl per liter.

EXERCISES

Making use of the data given and the table of atomic weights on page 600, solve the following problems:

1. Calculate the molecular weights of $\underset{\text{ozone}}{O_3}$, $\underset{\text{nitrogen}}{N_2}$, $\underset{\text{carbon dioxide}}{CO_2}$, $\underset{\text{hydrogen chloride}}{HCl}$, and $\underset{\text{borax}}{Na_2B_4O_7}$.

2. What is the specific gravity of $\underset{\text{ammonia}}{NH_3}$, $\underset{\text{chlorine}}{Cl_2}$, $\underset{\text{hydrogen}}{H_2}$, $\underset{\text{nitrogen}}{N_2}$, $\underset{\text{carbon dioxide}}{CO_2}$?

3. What is the vapor density of $\underset{\text{oxygen}}{O_2}$, $\underset{\text{carbon monoxide}}{CO}$, $\underset{\text{sulphur dioxide}}{SO_2}$, $\underset{\text{acetylene}}{C_2H_2}$, $\underset{\text{nitrous oxide}}{N_2O}$?

4. Calculate the weight of one liter of oxygen, nitrogen, carbon dioxide, ammonia, acetylene.

5. How many pounds of combined nitrogen are there in one ton of sodium nitrate, $NaNO_3$?

6. A cubic foot of water weighs 62.5 pounds. A cubic foot of cast iron weighs 462.5 pounds. What is the specific gravity of cast iron?

7. The specific gravity of lead is 11.3. Calculate the weight of 1 cubic foot of lead.

8. The specific gravity of concentrated sulphuric acid is 1.84. How many cubic feet are there in 1 ton of sulphuric acid?

9. Oak is 0.8 as heavy as water. What does a cubic foot of oak weigh?

10. Cork is 0.3 as heavy as oak; what is its specific gravity?

11. How many pounds of hydrogen and how many pounds of oxygen can be obtained by the decomposition of 50 pounds of water?

12. Salt and sulphuric acid react to form hydrogen chloride and sodium sulphate. How much salt would be consumed in the preparation of 20 pounds of sodium sulphate?

13. What is the percentage composition of ammonium sulphate $(NH_4)_2SO_4$?

14. When nitric acid is added to calcium carbonate, carbon dioxide, water, and calcium nitrate are formed according to the equation:

$$\underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{nitric acid}}{2\,HNO_3} \longrightarrow \underset{\text{calcium nitrate}}{Ca(NO_3)_2} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

How many cubic feet of carbon dioxide would be liberated from 5 pounds of calcium carbonate by the action of sufficient nitric acid?

15. When water is added to calcium carbide, calcium hydroxide and acetylene result:

$$\underset{\text{calcium carbide}}{CaC_2} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{calcium hydroxide}}{Ca(OH)_2} + \underset{\text{acetylene}}{C_2H_2}$$

What weight of calcium carbide would be required for the production of 2500 cubic feet of acetylene? What weight would be required if the calcium carbide were only 87 % pure?

16. What volume of oxygen would be required for the complete combustion of 1000 cubic feet of acetylene? Air contains 21 % of oxygen. What volume of air would be required?

17. What volume of carbon dioxide would be obtained by the complete combustion of 1000 cubic feet of marsh gas?

$$\underset{\text{marsh gas}}{CH_4} + \underset{\text{oxygen}}{2\,O_2} \longrightarrow \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{steam}}{2\,H_2O}$$

18. How much iron could be obtained from 200 tons of an ore containing 90 % of ferric oxide, Fe_2O_3?

19. What volume of hydrochloric acid having a specific gravity of 1.2, and what volume of water, would be required to make 1 liter of hydrochloric acid having a specific gravity of 1.1?

20. A merchant wants to prepare 5 liters of ammonia water with a specific gravity of 0.96 by diluting ammonia water having a specific gravity of 0.9. What volume of the concentrated ammonia water and what volume of water should he use?

21. Calculate the number of grams of each of the following compounds contained in its normal solution: HNO_3, H_2SO_4, $H(C_2H_3O_2)$, KOH, $Ca(OH)_2$, Na_2SO_4.

22. 21 cubic centimeters of a normal solution of nitric acid were required to neutralize 15 cubic centimeters of a solution of potassium hydroxide. How many grams of KOH per liter did the solution of potassium hydroxide contain?

23. 15.2 cubic centimeters of fifth-normal sulphuric acid were required to neutralize 18.7 cubic centimeters of a solution of ammonium hydroxide. What was the concentration of the ammonium hydroxide solution?

24. 16.3 cubic centimeters of half-normal sodium hydroxide solution were required to neutralize 10.5 cubic centimeters of a solution of sulphuric acid. Calculate the concentration of the sulphuric acid.

PHYSICAL CONSTANTS
OF THE IMPORTANT ELEMENTS

ELEMENT.	SYMBOL.	ATOMIC WEIGHTS.		VALENCE.	SPECIFIC GRAVITY.		MELTING POINT.	BOILING POINT.
		Approximate.	Exact O = 16.		Water = 1.	Air = 1.	° C.	° C.
Aluminum	Al	**27**	27.1	**III**	2.7		657	2200
Antimony	Sb	**120**	120.2	**III V**	6.6		630	1600
Argon	A	**40**	39.88	——		1.38	−188	−186
Arsenic	As	**75**	74.96	**III V**	5.7		. . .	<360 volatile
Barium	Ba	**137**	137.37	**II**	3.8		850	950
Bismuth	Bi	**208**	208.0	**III V**	9.7		269	1436
Boron	B	**11**	11.0	**III**	2.4		infusible	3500
Bromine	Br	**80**	79.92	**I**	3.1		−7.3	59
Cadmium	Cd	**112**	112.4	**II**	8.6		322	778
Calcium	Ca	**40**	40.09	**II**	1.8		about 780	. . .
Carbon	C	**12**	12.00	**IV**	amorphous 1.4–1.9		infusible	3500
Chlorine	Cl	**35.5**	35.46	**I**		2.49	−102	−33.6
Chromium	Cr	**52**	52.0	**II III VI**	6.9		1520	. . .
Cobalt	Co	**59**	58.97	**II**	8.7		1750	. . .
Copper	Cu	**63.6**	63.57	**I II**	8.9		1065	2100
Fluorine	F	**19**	19.0	**I**		1.26	−223	−187
Gold	Au	**197**	197.2	**I III**	19.3		1062	2500
Helium	He	**4**	3.99	——		0.13	−270	−267
Hydrogen	H	**1**	1.008	**I**		0.07	−256.5	−252
Iodine	I	**127**	126.92	**I**	4.9		113	184
Iron	Fe	**56**	55.85	**II III**	7.8		1550	. . .
Lead	Pb	**207**	207.1	**II IV**	11.3		327	1580

ELEMENT.	SYMBOL.	ATOMIC WEIGHTS.		VALENCE.	SPECIFIC GRAVITY.		MELTING POINT.	BOILING POINT.
		Approximate.	Exact O = 16.		Water = 1.	Air = 1.	° C.	° C.
Lithium	Li	**7**	6.94	**I**	0.59		186	<1400
Magnesium	Mg	**24**	24.32	**II**	1.7		632	1100
Manganese	Mn	**55**	54.93	**II IV**	7.4		1247	. . .
Mercury	Hg	**200**	200.0	**I II**	13.6		−38.8	357
Nickel	Ni	**58.7**	58.68	**II**	8.7		1452	. . .
Nitrogen	N	**14**	14.01	**III V**		0.96	−214	−195
Oxygen	O	**16**	16.00	**II**		1.10	<−218	−182
					yellow		yel	low
Phosphorus	P	**31**	31.04	**III V**	1.8		44.1	290
Platinum	Pt	**195**	195.2	**IV**	21.5		1760	. . .
Potassium	K	**39**	39.10	**I**	0.87		62.5	667
Silicon	Si	**28**	28.4	**IV**	2.4		1200	3500
Silver	Ag	**108**	107.88	**I**	10.5		961	2050
Sodium	Na	**23**	23.0	**I**	0.97		97.6	877
Strontium	Sr	**87**	87.63	**II**	2.5		900	white heat
							rhombic	
Sulphur	S	**32**	32.07	**II IV VI**	2.0		114.5	444.6
Tin	Sn	**119**	119.0	**II IV**	7.0–7.3		232	1525
Zinc	Zn	**65**	65.37	**II**	7.1		419	918

INDEX

References are to pages. Heavy-face numerals indicate the principal reference.

- **Abrasives** 416, **461**
- **Accumulator**, chloride 443
- **Acetate of lime** 375
- **Acetic acid** 20, 225
- **Acetone** 375
- **Acetylene** **111**, 137, 210
  - burners 137
  - series 210
- **Acid radical** 60
- **Acids** Chap. III, **14**
  - characteristics 18
  - common 18; Chap. XLIV, 534–546
  - definition 21
- **Actinic power** 349
- **Adulteration of foods** 263
- **Aëration of water** 174
- **Agriculture** Chap. XLV, **562**
- **Air**, character Chap. XV, **144**
  - composition 144
  - minor constituents 153
  - physical character 144
- **Alcohol**, as a fuel 107
  - denatured 217
  - ethyl 215
  - grain 215
  - methyl 214
  - wood 214
- **Alcoholic beverages** 218
- **Alcohols** 213
- **Aldehydes** 222
- **Alkalies**, definition 31
- **Alkyl radical** 214
- **Alloys** 197
- **Alpaca** 322
- **Alum baking powder** 273
- **Aluminum** **405**
  - bronze 201
  - extraction of 406
  - sulphate 558
- **Alundum** 463
- **Amalgams** 199, 410
- **Amendments**, soil 567
- **Ammonia** **549**
  - in air 153
  - in illuminating gas 377
  - liquid 550
  - preparation, synthetic 549
  - source 549
  - uses 550
  - water 30
  - water in cleaning 306
- **Ammonium**, chloride 40
  - group 30
  - hydroxide 30
  - sulphate 558
  - sulphate as fertilizer 567
- **Amorphous substances** 84
- **Amyloid** 233
- **Analin** 239
- **Anesthetics** 211, 237
- **Anhydrides**, acid, definition 69
- **Animal fibres** 322
- **Animal life**, relation to air 145
- **Anode** 3, **431**
- **Apatite in fertilizers** 575
- **Aquadag** 423
- **Aqua fortis** 20
- **Aqua regia** 539
- **Aromatic series** 238
- **Ash** 104
- **Atmosphere** 144
- **Atomic weights** 50
  - table of 600
- **Atoms** 47
- **Autogenous welding** 391

- **Babbitt metal** 199
- **Bacillus bulgaricus** 289
- **Bacteria**, in air 151
  - in milk 280
  - nitrifying 573
  - nitrogen fixing 571

Baking, of bread 269
  of meats 261
Baking powders **272**
  alum 273
  cream of tartar 272
  healthfulness of 273
  phosphate 272
Baking soda 558
Barometer 144
Bases Chap. IV, **23**
  action on organic matter 26
  action with acids 27
  characteristics 29
  definition 59
  nomenclature 63
  preparation 23
  uses 29
Basic lining, in furnaces 473
Bauxite 405
Beer 218
Bell metal 200
Benzene 238
Benzine 372
Benzoic acid 239
Benzol 238
Bessemer converter 472
Beverages, alcoholic 218
Binary compounds 55, 63
Blast furnace 468
Blast lamps Chap. XXXIII, **385**
Blaugas 139
Bleaching, of cotton 332
  of linen 332
  of silk 333
  of wool 333
Bleaching agents in laundering 310
Bleaching powder 555
Blowpipe, oxyacetylene 389
  oxyhydrogen 5, **387**
Blowpipes Chap. XXXIII, **385**
Blowtorch 386
Blueprints 344
Bluing 308
Boiler scale 184
Boilers, foaming in 186
  pitting of 186
Bone in fertilizers 575
Boneblack 236
Boracic acid 19
Borax 558
  in cleaning 306
Boric acid 19
Brandy 219
Brass **200**
Bread, baking of 269
  crust of 270
  kneading of 269
  porous structure of 268
  rising of 269
  salt-rising 271
Bread making Chap. XXXIV, **267**
  use of yeast in 268
Brick Chap. XLII, **506**
  fire 509
  glazed 509
  making of 506
  vitrified 508
Briquettes 105
Bristol brick 462
Broiling 261
Bronze 200
  aluminum 201
  phosphor 200
Building materials Chap. XLI, 490
Building stones 500
Bunsen burner 122
Burner, acetylene 137
  bunsen **122**
  fishtail 134
  gas 134
  gasoline **128**, 134
  gas range 124
  kerosene 133
  self-lighting 137
Burning Chap. X, **91**
  conditions necessary for 94
  definition 96
  energy change 96
  extinguishing 95
  simple types 9
Burnt sienna 359
Butane 206
Butter **295**
  adulterated 296
  process 296
  renovated 296
Butterine 296
Butyric acid 225

References are to pages.

Cadmium yellow 359
Calcium 25
  carbide 111, **417**
    rotary furnace 418
  hydroxide, formation of 25
  hypochlorite 554
  light 5, **388**
  oxide, manufacture 490
  sulphate 495
Candles 132
Canned goods 264
Caramel 237
Carat 202
Carbides 417, 419
Carbohydrates 232
  in foods 244
Carbolic acid 238
Carbon compounds Chaps. XIX, XX, **205**
Carbon dioxide, in air 149
  in beverages 219
  in bread making 268
  in fermentation 216
  in fire extinguishers 95
Carbon disulphide 424
Carbon monoxide 93, **117**
Carbon tetrachloride 212
Carbonates as ores 403
Carborundum 419
  for cleaning metals 463
Cashmere 322
Cassiterite 413
Cast iron 468, 485
Cathode, definition 3, **431**
Caustic potash 29, 554
Caustic soda 29, 553
Cave formation 182
Cell, Daniell 439
  dry 441
  Exide 443
  gravity 440
  Leclanché 441
  sal-ammoniac 440
  storage 442
Cells, polarization in 439
  primary 438
Celluloid 233
Cellulose **232**, 323
Cement Chap. XLI, **490**
  coating for iron 457
  hydraulic 496
    manufacture 496
  Portland 496
  setting of 498
Centrifugal filters 162
Champagne 219
Charcoal 347
Cheese **297**
  American 298
  cottage 297
Chemical calculations Chap. XLVI, **588**
Chemical change 1
Chemical glassware 528
Chemical problems, weight 589
  weight and volume 590
  volume 592
Chemical purification Chap. XVI, 157
Chemicals, commercial Chap. XLIV, **533**
  analyzed 534
  C. P. 534
  crude 534
  purity 533
  technical 534
Chile saltpeter 41
China **510**
  English 514
  Sèvres 514
Chinese wood oil 360
Chloride accumulator 443
Chloride of lime 555
Chlorine, in bleaching 310, 331, **332**
  in water purification 180
  process for gold 411
Chloroform 211
Chrome steel 487
Chrome yellow 358
Citric acid 18
Clay 506
Cleaning, dry 309
Cleaning and laundering Chap. XXVI, **302**
Coagulation, water purification by 179
Coal **102**
  cannel 105
  distillation of Chap. XXXII, **376**
  gas 108, 377

References are to pages.

Coatings, protective, for iron 456
Cobalt blue 358
Coin alloys 202
Coke 376
Collodion 233
Colored glass 527
Coloring in foods 263
Color photography 349
Combination, direct Chap. II, **8**
  definition 73
Combustion, ordinary **91**
  products of 93
  spontaneous 97
Compound, binary 55, 63
  definition 6
Concrete 498
Conduction of electricity 430
Conductivity of metals 192
Contact process for sulphuric acid 540
Converter, Bessemer 472
Cooking of foods Chap. XXII, **260**
Copper, in combination with sulphur 8
  corrosion of 454
  electrolytic refining of 447
  sulphate 38
Cordials 219
Corrosion of metals Chap. XXXVIII, **452**
  prevention of 454
Cotton 323
  mercerized 324
Cream, butter, cheese Chap. XXV, **293**
Cream 293
  whipped 293
Cream of tartar 272
Crocus, for polishing 463
Crops, common, constituents of 584
Croton water, analysis 169
Cryolite 406
Crystallization 82
  definition 165
  purification by 163
Cupola furnace 479
Cyanamid 567
Cyanide process for gold 411

Daniell cell 439
Decomposition, direct, definition 73
  of mercuric oxide 2
  of water 3
Definite proportions, law of 46
Denatured alcohol 217
Destructive distillation **374**
  of coal **376**
  of wood **374**
Dextrin 235
Dextrose 215
Diastase 215
Dicalcium phosphate 577
Digestion, enzymes in 263
Disease, transmission by water 171
Dishes, manufacture 512
Disinfectants 223, 555
Dissociation theory 431
Distillation, definition 164
  destructive 374
    of coal **376**
    of wood **374**
  purification by 158
Driers, paint 363
Drop forgings 480
Dry cell 441
  cleaning 309
Ductility of metals 194
Dust in air 151
Dutch process for white lead 354
Dyes and dyeing Chap. XXIX, **336**
Dyes, acid 338
  basic 339
  direct developed 338
  direct for cotton 336
  modern 336
  sulphur 339
  vat 340
Dynamite 231
  gelatin 232

Edison storage cell 443
Electric furnaces Chap. XXXVI, **417**
Electricity, conduction of 430
Electrochemical series 58
Electrochemistry Chap. XXXVII, **430**
  development of 430

References are to pages.

Electrolysis, explanation of 432
  of water 3
Electrolytes 430
Electrolytic refining of metals 446
Electroplating **445**
  copper 445
  gold 448
  nickel 456
  silver 448
Electro-silicon 463
Electrotyping 446
Element, definition 6
  negative 56
  positive 56
Elements, physical constants 600
  symbols of 48
Elutriation 420
Emeraude green 359
Emery 463
Emulsion 85
Energy requirement in foods 246
Engine, automobile 401
  combustion in 400
Engines, gas Chap. XXXIV, **396**
  gasoline 400
  kerosene 400
Enzymes in digestion 263
Epsom salts 40
Equations, chemical, writing of Chap. VIII, **66**
Esterification 227
Esters 226
Etching of glass 521
Ethane 206
Ether 237
Ethereal salts 226
Ethyl alcohol 215
Ethylene 210
  series 209
Exide storage cell 443
Explosive mixture 133
Explosives, high 231, 234

Fats 244
Fatty acids 225
Feldspar 578
Fermentation 216
Fermented milk 288
Ferric oxide for polishing 463
Ferrous sulphate 558
Fertility of soil 562
Fertilizers **567**
  ammonium sulphate 567
  apatite 575
  bone 575
  calcium phosphates 576
  cyanamid 567
  fish scrap 569
  guano **569**, 575
  kainite 578
  lime nitrogen 567
  phosphatic slag 575
  phosphoric acid, available 577
    citrate soluble 577
    total 577
    unavailable 577
  potassium chloride 578
  potassium sulphate 578
  rock phosphate 574
  sodium nitrate 567
  terms used in market quotations 579
  wood ashes 578
Fibres, animal 322
  plant 322
Filters, centrifugal 161
Fire brick 509
Fire extinguishers 95
Fireplaces Chap. XII, **114**
Fires, methods of putting out 95
  method of starting 115
Fire test, kerosene 372
Fish oil 360
Fish scrap as fertilizer 569
Fixation of nitrogen 570
Flame **102**, 132, 134
  bunsen 123
  hottest part 123
  oxidizing 123
  reducing 123
Flashing point 133
Flour, wheat 267
Flux 468
Foaming in boilers 186
Foods Chap. XXI, **242**
  adulteration 263
  canned 264
  colorings in 263
  cooking of 260
  digestion of 262

References are to pages.

- **Foods** — *Continued*
  - energy values 246
  - mineral constituents 250
  - preservatives in 263
  - protein requirement 248
  - purposes of 242
  - quantity required 246
  - substitution in 264
  - tables 253
  - values 244
- **Forgings**, drop 480
- **Formacone** 223
- **Formaldehyde** 223
- **Formalin** 223
- **Formic acid** 225
- **Formulas** 49
  - chemical, organic 225
- **Fractional distillation** . . . 369
- **Freezing**, purification by . . 160
- **Fructose** 215
- **Frying meats** 262
- **Fuels** . . . . . . Chap. XI, **101**
  - characteristics 101
  - definition 92, **101**
  - gaseous 108
  - liquid 105
  - solid 101
- **Furnace**, blast for iron . . . 468
  - cupola 479
  - electric . . . Chap. XXXVI, **417**
    - Heroult 425
    - laboratory 417
    - rotary carbide 418
    - tin 425
  - glass 519
  - hot air 119
  - open hearth 474
  - reverberatory 412
- **Fusibility of metals** 195
- **Fusible metals** 198

- **Gallic acid** 315
- **Gallotannic acid** 315
- **Galls for ink** 314
- **Galvanized iron** 456
- **Gas**, acetylene 111
  - arc 136
  - Blaugas 139
  - burners 134
  - coal 108
  - illuminating **377**
  - lighters 137
  - mantles 136
  - natural 110
  - oil 139, **371**
  - Prest-O-Lite 138
  - producer 110, **398**
  - range 123
  - stoves . . . . Chap. XIII, **122**
  - water 109, **381**
  - weight of a liter 589
- **Gas engines** . Chap. XXXIV, **396**
- **Gases**, purification of 157
  - solubility 85
- **Gasoline** 106, **373**
  - engines 400
  - lights 134
  - stoves . . . Chap. XIII, 122, 128
- **Gelatin dynamite** 232
- **German silver** 201
- **Giant powder** 232
- **Gin** 219
- **Glacial acetic acid** 20
- **Glass** . . . . . Chap. XLIII, **516**
  - aging of 522
  - blowing 523
  - Bohemian 516, 518
  - chemical properties 520
  - colored 527
  - common 516
  - cut 525
  - etching of 521
  - flint, composition . . . 517, 518
  - furnace 519
  - Jena 529
  - materials for 517
  - nature 516
  - optical 526
  - physical properties 522
  - plate 525
  - pressed 524
  - window, composition . . . 516, 518
    - manufacture 523
- **Glauber's salt** 40
- **Glazes**, pottery 511
- **Glucose sugar** (dextrose) . . 215
- **Gluten** 267
- **Glycerin** 229
- **Gold**, amalgamation of 410
  - chlorine process for 411

References are to pages.

Gold — *Continued*
- cyanide process for 411
- electrolytic separation from silver 447
- extraction of **410**
- panning of 410

Grain alcohol 215
Granite 501
Graphite, artificial 421
- deflocculated 423

Gravity cell 440
Green vitriol 558
Guano **569**, 575
Gun cotton 233
Gypsum in agriculture . . 583

Hartshorn, spirits of 30
Heroult electric furnace . . 425
Hollow tile 509
Humidity, relative 151
Hydraulic cement 496
Hydrocarbons **205**
- acetylene series 210
- aromatic series 238
- ethylene series 209
- methane series 206
- paraffin series 207
- unsaturated 209

Hydrochloric acid . . . 19, **534**
- commercial 535
- manufacture **534**
- properties 535
- uses of 536

Hydrofluoric acid 521
Hydrogen, electrolytic, manufacture 434
- peroxide 556
- preparation **3**
- properties 4

Hydrogenation of oils . . . 228
Hypo 558
Hypochlorites 554

Ice cream 294
Illuminating gas **377**
Illumination **140**
- principles of 140
- values 140

Indian red 357
Infusorial earth 461
Ink . . . . . Chap. XXVII, **314**
- copying 319
- India 317
- iron 315
- logwood 316
- nigrosin 317
- printers' 319
- red 318
- sepia 318

Invertase 216
Iodine, combination with mercury 8
Iodoform 212
Ion 431
Ionization theory 431
Iron . . . . Chap. XL, **468**
- blast furnace 469
- cast 468
- casting of 479
- hardness of 482
- magnetic properties 484
- malleability 482
- pig 471
- Russia 458
- rust 455
- rusting of **453**, 455
- tenacity 482
- uses 485
- wrought 472
  - manufacture 478

Japan drier 363
Javelle water 310, 554

Kainite as fertilizer 578
Kaolin 506
Kerosene 107
- fire test 372

Kiln, lime 492
Kindling point 92
Kitchen range 118
Kumiss 288

Lakes 357
Lamp, blast . . Chap. XXXIII, **385**
- kerosene 132

Lanolin 328
Laundering . . Chap. XXVI, **302**
Lead, acetate 558

References are to pages.

- **Lead** — *Continued*
  - burning 388
  - corrosion of 454
  - extraction of **412**
  - pencils 423
  - white 354
    - sublimed 355
- **Leavening**, by carbon dioxide 270
  - salt-rising 271
  - sour milk 274
  - yeast 268
- **Leclanché cell** 441
- **Levulose** 215
- **Light**, calcium 5
- **Lights**, oil and gas Chap. XIV, 132
- **Lignite** 105
- **Lime** Chap. XLI, **490**
  - air slaked 494
  - kiln, rotary 492
  - kiln, vertical 490
  - light 388
  - manufacture 490
  - slaked 29
  - slaking of 494
  - unslaked 490
- **Limestone** 502
  - in agriculture 528
- **Linen** 327
- **Linseed oil** 359
- **Liqueurs** 219
- **Litharge** 359
- **Lithophone** 356
- **Lubricating oils** **373**, 423
- **Lye** 29

- **Magnalium** 202
- **Magnesium**, combination with oxygen 9
  - sulphate 40
- **Malleability of iron** 192
- **Malt** 215
- **Maltose** 215
- **Manganese**, extraction of 408
  - steel 486
- **Mantles**, gas 135
- **Marble** 502
- **Marsh gas** 207, **208**
- **Matches** 92
- **Meats**, baking of 261
  - broiling 261
  - frying 262
  - roasting 262
  - stewing 261
- **Melting points of elements** 602
- **Mercerized cotton** 324
- **Mercuric oxide**, decomposition 2
- **Mercury**, extraction of 404
  - combination with iodine 8
- **Metal**, Babbitt 199
  - bell 200
  - type 201
- **Metallic oxides**, action with acids 37
- **Metals**, bearing 199
  - chemical cleaning of 464
  - cleaning of Chap. XXXIX, **461**
  - conductivity 192
  - corrosion Chap. XXXVIII, **452**
  - ductility 194
  - extraction of Chap. XXXV, **403**
  - fusibility 195
  - fusible 198
  - hardness 196
  - malleability 192
  - self-protective 454
  - typical properties Chap. XVIII, **192**
- **Methane** 207, **208**
  - series 206
- **Methyl alcohol** 214
  - chloride 211
- **Milk** Chap. XXIV, **278**
  - bacteria in 280
  - certified 283
  - composition 278
  - condensed 286
  - evaporated 285
  - fermented 288
  - handling of 279
  - homogenized 287
  - keeping sweet 281
  - modified 283
  - necessity for pure 278
  - Pasteurized 281
  - powdered 287
  - preservatives in 281
  - putrefaction of 280
  - sources 279
  - souring of 280
  - sterilized 285

- **Mineral constituents of foods** 250
  - definition 403
- **Mirrors** 200
- **Miscibility** 84
- **Mixtures**, explosive 133
- **Modified milk** 283
- **Mohair** 322
- **Molecular weight** 50
  - calculation of 588
- **Molecules** 48
- **Mono-calcium phosphate** 577
- **Monochlormethane** 211
- **Mordant** 339
- **Mortar** 494
- **Multiple proportions**, law of 47
- **Muriatic acid** 19, **535**

- **Naphtha** 371
- **Natural gas** 110
- **Neutralization**, defined 28, 42
  - explanation of 436
  - production of salt by 36
- **Nickel**, plating on iron 456
  - steel 486
- **Niter** 39
- **Nitrates** 567, 571
- **Nitric acid** 20, **536**
  - from air 539
  - in air 153
  - manufacture **536**, 539
  - properties 537
  - uses 538
- **Nitrification** 573
- **Nitrifying bacteria** 573
- **Nitrocellulose** 233
- **Nitrogen** 149
  - fertilizers 567
    - choice of 573
  - fixation of 570
  - in air 149
- **Nitrogen fixing bacteria** 571
- **Nitroglycerin** 231
- **Nomenclature** Chap. VII, **55**
- **Normal solutions** 594

- **Ochre**, yellow 359
- **Oil**, drying 97
  - flash point 133
  - gas 139, **371**
  - lamp 132
  - of vitriol 20
  - petroleum, heavy 370
    - intermediate 371
    - light 370
- **Oildag** 423
- **Oils**, hydrogenation of 228
- **Oils**, painting Chap. XXXI, **353**
  - Chinese wood 360
  - fish 360
  - linseed 359
  - poppy 360
- **Oleic acid** 229
- **Oleomargarine** 296
- **Open hearth furnace** 474
- **Optical glass** 526
- **Ore**, definition 403
- **Ores**, carbonates 403
  - sulphides 404
- **Organic acids** 224
- **Organic compounds**, nature of 205
- **Oxalic acid** 464
- **Oxidation** Chap. X, **91**
  - slow 96
- **Oxides**, carbon dioxide 10, **91**, 116
  - carbon monoxide 93, **117**
  - magnesium 9
  - mercuric 2
  - phosphorus 10
  - tin 9
- **Oxyacetylene blowpipe** 389
  - cutting 393
- **Oxy-Blaugas** 392
- **Oxygen** 2, **5**
  - electrolytic 434
  - in air 144
  - nascent 67
  - preparation 2, **3**
  - properties 2, **5**
  - standard for reacting weights 45
- **Oxyhydrogen blowpipe** 5
- **Ozone**, in air 154
  - water purification 180

- **Paint driers** 363
- **Paints** Chap. XXXI, **353**
  - enamel 362
  - floor 362
  - for iron 457
  - ready mixed 361
  - water 360

References are to pages.

Palmitic acid 225
Paper, parchment 233
  waterproof 232
Paraffin 373
  oil distillate 371, **373**
  series 207
Paris green 359
Pastry 275
Peat 105
Pencils, lead 423
Pentane 206
Petroleum 105
  cracking of 373
  crude 368
  distillation . Chap. XXXII, **368**
  purification of 372
  refining 105, 368
Phosphates 574
Phosphor bronze 200
Phosphoric acid in fertilizers 577
  available 577
  citrate soluble 577
  total 577
  unavailable 577
Phosphorus, combined with oxygen 10
  forms of 10
  in fertilizers 574
Photographic plates . . . 346
  prints 348
  toning 348
Photography . . Chap. XXX, **344**
  color 349
  developer 345
  fixer 345
  sensitive substance 345
  sensitizer 345
Physical constants, table of . 600
Pig iron 471
Pigments . . . Chap. XXXI, **353**
  blue 358
  colored 357
  definition 353
  green 359
  inert 356
  red 357
  white 354
  yellow 358
Pitting of boilers 186
Plant fibres 322
Plant life, relation to air . . 145
Plants, elements essential to . 562
Plaster 495
  of Paris 495
Plate glass 525
Plates, orthochromatic . . . 349
  photographic 346
Plating, copper 445
  electrolytic 448
  gold 448
  silver 448
Plugs, automatic sprinkler . . 198
  fusible 198
  safety 198
Polarization, prevention of . . 439
Polishing powders **461**
Porcelain 511, **512**
  soft 511
Portland cement 496
Potash, caustic 29
Potassium carbonate, manufacture of 550
  chlorate 555
  chloride 38
    as fertilizer 578
  cyanide 558
  dichromate 558
  feldspar 578
  ferrocyanide 558
  hydroxide 29
  nitrate 39
  permanganate 558
  sulphate as fertilizer 578
Pottery . . . . Chap. XLII, **506**
  glazes for 511
  unglazed 509
  varieties 510
Powder, baking **272**
  giant 232
  polishing 461
  silica 462
  smokeless 234
Precipitates, purification by washing 161
  purification by filtration . . 161
  resulting from action of ions . 437
Precipitation 83
  definition 165
  purification by 162

References are to pages.

- **Preservatives in foods** 263
- **Prest-O-Lite** 138
- **Primary cells** 438
- **Prints**, photographic 348
- **Producer gas** 398
- **Propane** 206
- **Propionic acid** 225
- **Protein requirement in foods** 248
- **Proteins** 243
- **Protoplasm** 243
- **Prussian blue** 358
- **Puddling process** 478
- **Pumice for polishing** 462
- **Purification**, by crystallization 163
  - by distillation 158
  - by freezing 160
  - of gases 157
  - of solids 160
  - by sublimation 161
  - by washing 161
  - of water 173
- **Purity**, chemical 157
- **Putz pomades** 463
- **Pyroligneous acid** 375
- **Pyroxylin** 233

- **Quartz** 461, 517
- **Quicklime** 25, **494**

- **Radical**, acid 60
  - ammonium 30
- **Range**, gas 123
  - kitchen 118
- **Reacting weights** 45
- **Red lead in paints** 357
- **Refining of metals by electrolysis** **446**
- **Replacement**, double, definition 73
  - simple, definition **13**, 73
- **Reverberatory furnace** 412
- **Roasting meats** 262
- **Rock phosphate** 574
- **Rouge** 463
- **Rum** 219
- **Russia iron** 458
- **Rust**, iron **453**

- **Sal ammoniac** 40, 41
- **Salt** 33
- **Saltpeter** 39
  - Chile 39
- **Salt rising bread** 271
- **Salts** Chap. V, **33**
  - acid 61
  - basic 61
  - definition 21
  - effect on litmus 40
  - ethereal 226
  - formation by replacement 18, **37**
    - by neutralization 36
    - from metallic oxides 37
  - important, tables of **41**, **558**
- **Sand** 494, 517
- **Sand filters for water** 177
- **Sandstone** 503
- **Saponification** 228, 230
  - definition 239
- **Scale**, boiler 184
- **Schweitzer's reagent** 232
- **Sedimentation**, water purification 179
- **Segger** 512
- **Seltzer** 86
- **Series**, electrochemical 58
- **Shortening** 275
- **Sienna**, burnt 359
- **Silica**, for polishing 462
  - ware 529
- **Silicon carbide** 419
  - dioxide 461
- **Silk** **329**
  - artificial 325
  - Chardonnet 325
  - conditioning 331
  - ecru 331
  - Pauly's 326
  - viscose 326
  - weighted 331
- **Silver**, cleaning of 464
  - bromide in photography 346
  - corrosion of 454
- **Slag** 468
  - phosphatic, fertilizers 575
- **Slaked lime** 29
- **Smokeless powder** 234
- **Soap** **302**
  - adulterations in 305
  - floating 305
  - green 305

References are to pages.

- **Soap** — *Continued*
  - manufacture of 302
  - modified bases 27
  - powdered 306
  - scouring 306
  - shaving 306
- **Soda**, washing 306
- **Sodium bicarbonate** **551**, 558
  - benzoate 239
  - carbonate 550
    - Solvay process **550**
  - chloride 33
    - electrolysis of 432
  - hydroxide 23, **552**
    - Castner process 552
  - hypochlorite 554
  - nitrate 39
    - as fertilizer 567
  - peroxide 557
  - silicate 558
  - sulphate 39
  - tetraborate 558
  - thiosulphate 558
- **Softening of water** **187**
  - plants for 189
- **Soil**, amendments 567
  - fertility 562
  - reserve material in 566
  - stimulants 582
- **Soils**, composition 565
  - origin 564
- **Solder** 198
- **Solids**, purification 160
- **Solute** 77
- **Solutions** Chap. IX, **76**
  - calculations for specific gravity 593
  - concentrated 79
  - definition 77
  - dilute 78
  - effect of temperature **82**, **85**
    - of pressure 86
  - nature 76
  - normal 594
  - saturated 80
- **Solvay process** 550
- **Solvent** 77
- **Specific gravity of a gas** 588
- **Spirits of hartshorn** 30
- **Spontaneous combustion** 97, 99
- **Spots**, removal 310
- **Stains**, for wood 362
  - oil 363
  - removal of 310
  - varnish 363
  - water 362
- **Starch** 234
- **Starching** 308
- **Steam stills**, petroleum 371
- **Stearic acid** 225
- **Steel** Chap. XL, **468**
  - alloys 486
  - Bessemer **472**
  - casting of 479
  - chrome 487
  - crucible **475**
  - electric furnace 476
  - electric refining 425
  - half-hard 472
  - hard 472
  - hardness of 482
  - high carbon 472, 485
  - high grade 475
  - low carbon 472, 485
  - magnetic properties of 484
  - malleability of 482
  - manganese 486
  - medium carbon 472, 485
  - mild 472
  - nature of 471
  - nickel 486
  - open hearth **474**
  - soft 472
  - tempering 482
  - tenacity 482
  - tool 472
  - tungsten 486
  - uses 485
  - vanadium 487
- **Steels**, uses 485
  - alloy 486
- **Sterilization of water** **173**, 189
- **Stewing meats** 261
- **Stones**, building 501
- **Stoneware** 511
- **Storage cells** **442**
  - chloride accumulator 443
  - Edison 443
  - Exide 443
  - lead 442

- **Stoves** Chap. XII, **114**
  - coal 115
  - gas Chap. XIII, 122, 123
  - gasoline Chap. XIII, 122, 128
  - kitchen 118
  - wood 117
- **Sublimation**, definition 164
  - purification by 161
- **Substitution in foods** 264
  - products 210
- **Sucrose** 236
- **Sugar** 236
  - barley 237
  - cane 236
  - glucose (dextrose) 215
- **Sugar of lead** 558
- **Sulphides as ores** 404
- **Sulphur** **546**
  - combination with copper 8, 91
    - with oxygen 91
  - extraction of 546
  - Louisiana deposits 547
  - uses 549
- **Sulphuric acid** 20, **539**
  - chamber process 541
  - chemical properties 544
  - contact process 439
  - physical properties 544
  - uses 546
- **Superphosphate of lime** 576
- **Supporter of combustion** 91
- **Suspension** 78
- **Symbols** 48
- **Synthesis** 11

- **Tables**, food 253
  - elements, physical constants of 600
- **Tannic acid** **19**, 315
- **Tempera painting** 360
- **Temperature**, kindling 92
- **Tempering of steel** 482
- **Terra cotta** 509
- **Textile materials** Chap. XXVIII, **322**
- **Thermit** 408
  - welding 408
- **Tile**, hollow 509
- **Tiles** 506
- **Tin chloride** 558
  - electric furnace 425
  - extraction of **413**
  - salt 558
  - ware 456
- **Toning**, photographic 348
- **Torch**, blow 386
  - gasoline 134
- **Tricalcium phosphate** 577
- **Trichlormethane** 211
- **Tungsten steel** 486
- **Turpentine** 364, 383
- **Type metal** 201

- **Ultramarine** 359
- **Unsaturated hydrocarbons** 208
- **Unslaked lime** 490

- **Valence** **55**
  - defined 62
  - important 56
  - of common elements 62
  - satisfaction of 58
- **Vanadium steel** 487
- **Vapor density** 589
- **Varnishes** 363
- **Vaseline** 373
- **Vehicle in paints** 353
- **Venetian red** 357
- **Ventilation** 146
- **Vermilion** 357
- **Vinegar** 226
- **Viscogen** 293
- **Vitriol**, blue 41
  - oil of 20
  - white 41

- **Washing**, clothes 307
  - precipitates 161
  - soda 306
- **Water** Chap. XVII, **167**
  - color 169
  - commercial electrolysis 434
  - Croton, analysis of 169
  - decomposition 2
  - electrolysis of 3, 433
  - hard **181**
    - action with soap 183
    - in chemical industries 186
    - permanent 183
    - temporary 182
  - natural content 167

References are to pages.

Water — *Continued*
odor and taste 170
pure and wholesome 169
purification **173**
aëration 174
chlorination 180
coagulation 179
cold 175
light 175
mechanical filters 177
mechanical processes 176
ozonization 181
sand filtration 177
sedimentation 179
soil filtration 175
softeners 188
softening 187
softening plants **189**
sources 167
sterilization 189
transmission of disease by 171
turbidity 78, 87, **170**
value of 167
vapor in air 150
Water gas **380**
enriched 381
Water glass 558
Water-proof paper 232
Weight relations Chap. VI, **44**
determination of 44
Weights, atomic 50
molecular 50
reacting 45
Welding, autogenous 391
electric 481
of iron 480
thermit 408
Whisky 219
White lead 354
sublimed 355
White metal 201
White vitriol 37
Whitewash 360
Whiting 465
Wines 218
Wood, as fuel 101
alcohol 214
ashes, as fertilizer 578
distillation of Chap. XXXII, 374
Wood's alloy 199
Wool 328
Wrought iron, manufacture of 478

Yeast 216
in bread making 268
Yellow ochre 359
Yellow prussiate of potash 558

Zinc, corrosion of 454
extraction of **404**
Zinc chloride 17, **37**
Zinc oxide, in paints 355
Zinc sulphate 17, **37**
Zymase 216

UNIVERSITY OF CALIFORNIA LIBRARY
BERKELEY
Return to desk from which borrowed.
This book is DUE on the last date stamped below.

MAR 26 1948
April 26 '48
4JAN'62DT
REC'D LD
JAN 3 1962
11May'65Th
REC'D LD
APR 27 '65 -7 PM

2Aug'65VIX
REC'D LD
SEP 29 '66 -2 PM

1–100m-9,'47(A5702s16)476

YB 16636

321445

QD37
B7

UNIVERSITY OF CALIFORNIA LIBRARY